

COMPRESSION FACTOR AND VAPOR LIQUID
EQUILIBRIUM CALCULATIONS :
CARBON DIOXIDE - HYDROCARBON SYSTEMS

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CERTIFICATE

It is certified that this work entitled
"Compression Factor and Vapor Liquid Equilibrium
Calculation: Carbon Dioxide-Hydrocarbon Mixtures"
has been carried out under my supervision and that
this has not been submitted elsewhere for a degree.

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A handwritten signature in black ink, appearing to read "V. Karuppasamy". The signature is fluid and cursive, with "V." on the left and "Karuppasamy" on the right.

— V. KARUPPASAMY

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(1) Lennard Jones Potential

<u>Mixtures</u>	<u>Composition</u>	<u>Temperature, °F</u>	<u>Pressure in psia</u>	<u>Page</u>
CO_2 -Ethane	0.2	160, 220, 280, 340, 400, 460	200, 400, 600, 800, 1000, 1250, 1500, 1750, 2000, 2250	30
	0.6	100, 160, 220, 280, 340, 400, 460	200, 400, 600, 800, 1000, 1750, 2000	33
	0.8	160, 220, 280, 340, 400, 460	200, 400, 600, 800, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 2750, 3000	36
CO_2 -Propane	0.2	220, 280, 340, 400, 460	200, 800, 1000, 1250	40
	0.4	220, 280, 340, 400, 460	200, 800, 1000, 1250	42
	0.8	160, 220, 280, 340, 400, 460	200, 400, 600, 800, 1000, 1250, 1500, 2000	44
CO_2 -N-Butane	0.2	340, 400, 460,	200, 400, 600, 800, 1000	47
	0.5	340, 400, 460	200, 400, 600, 800, 1000, 1250, 1500	48
	0.7	340, 400, 460	200, 400, 600, 800, 1000, 1250, 1500	50

(2) VLE Calculation

<u>Sl. No.</u>	<u>System</u>	<u>Temperature, °F</u>	<u>Pressure Range in psia</u>	<u>No. of points</u>	<u>Page</u>
1.	CO ₂ -Methane	-65.0	300-700	5	52
2.	"	-57.0	300-700	5	53
3.	"	-25.0	300-700	5	54
4.	CO ₂ -Propane	-40.0	15.0-145.0	4	55
5.	"	-4.0	34.0-285.0	5	56
6.	"	11.8	35.28-283.710	12	57
7.	"	32.0	67.0-507.0	6	58
8.	"	32.0	69.090-505.680	12	59
9.	"	40.0	79.0-566.50	12	60
10.	"	70.0	125.0-860.90	17	61
11.	"	100.0	188.7-1002.50	19	62
12.	"	130.0	237.50-992.00	16	63
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14.	CO ₂ -N-Butane	32.0	15.288-505.680	15	65
15.	"	69.78	59.976-1057.224	20	66
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NOmenclature

ρ	Molar density
β	Compression factor
β_{LJ}	Compression factor, augmented with L.J. potential
N	Avagadro's number in Chapter 2
β_{hs}	Compression factor for hard sphere molecule
σ	Hard sphere diameter, \AA
$u(r)$	Potential function
d	Equivalent hard sphere diameter
n	Number of Virial coefficients truncated for augmentation
B_2	Second Virial coefficient
B_3	Third Virial coefficient
B_m	Second Virial coefficient of the mixture
γ_m	Third Virial coefficient of the mixture
ω	Accentric factor
T_r	Reduced temperature
n_i	Number of moles of component i
f_i	Fugacity of component i
x	Molefraction
a_{ci}, b_{ci}, c_{ci} $a_i, b_i, c_i, \gamma_i, \omega_i$	Pure component parameters for DWR equation
T	Temperature
P	Pressure
K_i	Equilibrium vaporization ratio of component i
ϵ	Characteristic energy

CHAPTER 1

INTRODUCTION

1.1. Literature Review

The separation of liquid or gaseous multicomponent mixtures into pure components or into fractions of desired composition is a common need of the chemical industry, e.g. in the preparation of mixture of raw materials for further processing and the purification of reaction products, etc. One of the essential requirements for rational design of units in separation operations like distillation, absorption, extraction etc. is a knowledge of the governing phase equilibria.

The possible number of liquid and vapor mixtures in technological processes is incredibly large and it is unreasonable to expect that experimental vapor liquid equilibria will ever be available for a significant fraction of this number. Furthermore, obtaining reliable and accurate experimental data requires an appreciable experimental skill and experience. It is, therefore, an economic necessity to consider techniques for calculating phase equilibria for multicomponent mixtures from few experimental data. Such techniques should require only a limited experimental effort and whenever possible, should be based on a theoretical foundation to provide reliability for interpolation and extrapolation with respect to temperature, pressure and composition.

Equations of state are usually used for predicting vapor-liquid equilibrium and volumetric properties in the absence of experimental data. Following van der Waals' work in 1873, many variations of the semi-empirical PVT equations have been proposed and these continuing efforts extended over more than a century and voluminous articles on this subject exist in the literature. The subject received fresh inputs with the advent of computers.

All existing equations are practical modifications of either the Virial equation or the Hard Core equation or both. Two major equations of state that still continue to be modified are the Redlich-Kwong (RK) and Benedict-Webb-Rubin (BWR) equation.

Redlich and Kwong⁽¹⁾ formulated a two parameter equation in 1949. Since then numerous modified RK equations have been proposed by Redlich and Dunlop⁽²⁾, Chue and Trausnitz⁽³⁾; Wilson⁽⁴⁾, Zadvitch and Joffee⁽⁵⁾ and numerous others. Chaudron and Renon⁽⁶⁾, Vogl and Hall⁽⁷⁾ considered the parameters as polynomials in the inverse reduced temperature and, by regressing experimental data for pure components, obtained constants for 25 substances. However, one recent modification of this equation made by Soave⁽⁸⁾, known as the Soave-Redlich-Kwong (SRK) equation, has rapidly gained acceptance by the hydrocarbon processing industry because of the relative simplicity of the equation. The most evident weakness of the SRK equation is that it is applicable only upto the critical temperature even for simple fluids.

The BWR equation⁽⁹⁾ is one of the most elaborate equations of state. It was originally developed by considering the properties of hydrocarbons and is traditionally associated with these compounds. However, this has been applied also to non-hydrocarbons. In general, the BWR equation will predict pressures that are within 0.5 per cent of the true values and densities upto 1.8 times the critical density. Major deviations exist at $T_r = 1.03$ and above a reduced pressure of 1.1. This is not unexpected since it is in the low temperature-high pressure region that the deficiencies of the BWR equation are more apparent.

Benedict et.al.⁽⁹⁾ demonstrated the ability of their equation to successfully predict phase equilibrium data for the Methane-Butane system at high temperatures. Few years later the same group extended the equation to low temperature predictions of pure component vapor pressures by defining the pure component coefficient as a function of temperature.

Scotler and Benedict⁽¹⁰⁾ further extended the BWR equation to predict hydrocarbon-nonhydrocarbon systems. They discovered that even though pure component vapor pressures were accurately predicted, the calculated phase equilibrium for mixtures of the same pure components showed significant errors. The inaccuracies were said to be due to the inability of the mixing rules to describe system nonidealities. The solution to this problem was to make A_{ij} in the mixing rule a function of the binary nonidealities. Their modification of

the mixing rule consisted of introducing a binary interaction coefficient k_{ij} , which was back calculated from experimental phase equilibrium data. In this manner, the phase equilibrium behavior of Nitrogen-Methane system were accurately predicted. Turner and Alder⁽¹¹⁾, while working with natural gas systems, found that though predictions for wide boiling hydrocarbon-hydrocarbon mixtures could be accurately made at moderate and high temperatures, errors appeared at low temperatures. Their conclusion was that the mixing rules were the cause of these errors. Thus even for the prediction of a relatively close boiling system, Methane-Propane, at low temperatures, the original mixing rules were inadequate.

Orye⁽¹²⁾ successfully predicted phase equilibrium data for several wide boiling hydrocarbon-hydrocarbon and hydrocarbon-nonhydrocarbon systems by the modified mixing rule. For A_c Stotler and Benedict⁽¹⁰⁾, and Guganoni and Lee applied the modified BWR equation to the experimental data of CO₂-Ethane system.⁽²²⁾

Joffee and Zudkivitch⁽⁵⁾ and Kaminishi et.al.⁽¹⁴⁾ noted that vapor liquid equilibrium relationships for systems containing CO₂ and light hydrocarbons could not be well correlated by using an equation of state. However, it has been pointed out^(14,15) that a marked improvement in these calculations are obtained by applying a modified BWR equation of state with the correction factor m corresponding to the interaction parameter.

A generalized BWR equation proposed by Starling and San⁽¹⁶⁾, known as the BWRS equation, is able to predict the properties at reduced temperatures as low as $T_r = 0.3$ and reduced densities as high as $\rho_r = 3.0$. In this relation four coefficients are added to make it temperature sensitive. Later Nishizawa and Saito⁽¹⁷⁾ generalized the BWRS equation adding further four coefficients to predict thermodynamic properties at extremely low reduced temperatures, e.g., the vapor pressures of heavy hydrocarbons below a reduced temperature of 0.5.

1.2. Present Work

The present work involves calculation of vapor-liquid equilibria in binary systems of CO_2 with five light paraffins and Isobutane. The phase behavior of binary mixtures of CO_2 and light hydrocarbons has been investigated in some detail since the measurement of Kuenen in 1897, but there have been few vapor liquid equilibria studies in the low temperature range. Of more interest is the fact that these binaries do differ markedly in phase behavior from hydrocarbon systems because of the significant quadrupole moment of CO_2 as well as weak acid base complex formation with hydrocarbons.⁽¹⁸⁾ Comparison of experimental data with the modified RK equation^(19,20) provides a fairly good representation of the experimental data for each binary system. A modified BWR equation is also suitable for the study of CO_2 -hydrocarbon systems⁽¹²⁾ are of importance in secondary

recovery of petroleum reservoir fluids and in processing plants to remove solidified CO_2 either by absorption in amines or by molecular sieves.

The first part of the work applies the Augmented Duan and Jones Equation of State⁽²¹⁾ in calculating compression factors at various temperature and pressures for binary mixtures of CO_2 and hydrocarbon.

The second part of the study involves vapor liquid equilibrium calculations for CO_2 -hydrocarbon binaries using the modified EWR equation of state.

CHAPTER 2

THEORY

2.1. Augmented Lennard-Jones (L-J) Equation of State

An equation of state is developed by combining L-J equation with a truncated Virial equation like the Augmented Hard Sphere equation developed by Bierkowski⁽²³⁾. The Augmented Hard Sphere equation is a combination of the Hard Sphere Equation (meant for high density) and Virial Equation (restricted to low density) in order that a systematic combination of the two may lead to a quantitative description of all the densities. With this augmenting procedure, the Augmented L-J equation of state is of the form:

$$\begin{aligned} Z^{LJA} &= \sum_{i=1}^{\infty} B_i^{LJ} \rho^{i-1} + \sum_{i=1}^n (B_i - B_i^{LJ}) \rho^{i-1} \\ &= Z^{LJ} + \sum_{i=1}^n (B_i - B_i^{LJ}) \rho^{i-1} \end{aligned} \quad (1)$$

2.2. Lennard-Jones Equation of State

Considering the perturbation theory studied by Barker and Henderson⁽²⁶⁾; Verlet and Weis⁽²⁷⁾ presented equation of state for L-J fluid. It has been approximated by hard sphere with a temperature dependent diameter. The interaction between the atoms for L-J potential is

$$\phi(r) = 4 \epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}$$

The equation of state for L.J. fluid proposed by Verlet and Weis is as follows:

$$\frac{P}{P_{hs}} = \left(\frac{P}{P_{hs}} \right)_{hs} + \beta N \rho d^3 \phi_1 (N \rho d^3) + \beta^2 (N \rho d^3)^2 \phi_2 (N \rho d^3) \quad (2)$$

where $\phi_1 (N \rho d^3) = \sum_1^{\infty} b_n^1 (N \rho d^3)^n / n$ (3)

$$\phi_2 (N \rho d^3) = \sum_1^{\infty} c_n^1 (N \rho d^3)^n / n \quad (4)$$

Since molecular collisions become more energetic at higher temperatures, the interpenetration of the electronic clouds becomes deeper and hard core appears smaller. Barker and Henderson⁽²⁶⁾ suggested a rational definition of the hard core diameter d as a function of temperature given by:

$$d = \int_0^{\sigma} (1 - e^{-\epsilon u(r)}) dr \quad (5)$$

$$d = \int_0^{\sigma} \left\{ 1 - e^{-\frac{4}{\pi \epsilon} \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right\}} \right\} dr \quad (6)$$

The equation proposed by Carnahan and Starling⁽²³⁾ is:

$$z_{hs} = \frac{1 + n^2 + n^2 - n^3}{(1 - n)^3} \quad (7)$$

where $n = \frac{\pi}{6} N \rho \sigma^3$, $T^* = KT/\epsilon$

Using equations (3), (4), (6) and (7), the expansion in the power series about density, i.e., equation (2) reduces to:

$$\begin{aligned}
 \frac{P}{RT} = Z^{LJ} = & 1 + \left(\frac{2}{3} \pi N d^3 + \beta b_1^1 N d^3 \right) r + \left\{ 10 \left(\frac{\pi}{6} N d^3 \right)^2 + \right. \\
 & \left. \beta b_2^1 N^2 d^6 + \beta^2 c_1^1 N^2 d^6 \right\} r^2 + \left\{ 18 \left(\frac{\pi}{6} N d^3 \right)^3 + \right. \\
 & \left. \beta^2 c_2^1 (N d^3)^3 \right\} r^3 + \left\{ 28 \left(\frac{\pi}{6} N d^3 \right)^4 + \beta^2 c_3^1 (N d^3)^4 \right\} r^4 + \\
 & \left\{ 19 \left(\frac{\pi}{6} N d^3 \right)^5 + \beta b_5^1 (N d^3)^5 \right\} r^5 + 5 \left(\frac{\pi}{6} N d^3 \right)^6 r^6 - \\
 & \left\{ 15 \left(\frac{\pi}{6} N d^3 \right)^7 - \beta b_7^1 (N d^3)^7 \right\} r^7 + \beta b_{27}^1 (N d^3)^{27} r^{27} + \\
 & \left. \beta^2 c_{28}^1 (N d^3)^{29} \right\} r^{29} \quad (8)
 \end{aligned}$$

$$\text{Here } \beta = \frac{1}{T^*}$$

$$\begin{aligned}
 b_1^1 &= -5.851 & c_1^1 &= -1.27 \\
 b_2^1 &= -5.757 & c_2^1 &= 7.438 \\
 b_5^1 &= 16.239 & c_3^1 &= -8.938 \\
 b_7^1 &= -5.966 & c_{28}^1 &= 197.24 \\
 b_{27}^1 &= -81.585
 \end{aligned}$$

The augmented L.J. equation of state truncated after the third Virial coefficient is:

$$Z^{LJA} = Z^{LJ} + (B_2 - B_2^{LJ}) r + (B_3 - B_3^{LJ}) r^2 \quad (9)$$

From equation (8),

$$B_2^{LJ} = \frac{2}{3} \pi N d^3 + \beta b_1^1 N d^3 \quad (10)$$

$$B_3^{LJ} = \left\{ 10 \left(\frac{\pi}{6} N d^3 \right)^2 + \beta b_2^1 (N d^3)^2 + \beta^2 c_1^1 (N d^3)^2 \right\} \quad (11)$$

Tsoukpolous⁽²³⁾ modified the Pitzer and Curl relation for second Virial coefficient and the same is used to calculate the second Virial coefficient of CO_2 and light hydrocarbons. The analogous correlation is given by:

$$\frac{B_2^0}{T_c} = f^{(0)} + \beta f^{(1)} \quad (12)$$

$$f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1585}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad (13)$$

$$f^{(1)} = 0.0657 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (14)$$

Third Virial coefficients for Methane, Ethane and Propane is calculated by Pope's⁽²⁹⁾ generalized correlation for normal fluids given by:

$$\frac{C}{V_c^2} = C^{(0)} + \omega C^{(1)} + \omega^2 C^{(2)} \quad (15)$$

$$C^{(0)} = 107.08524180 - \frac{2444.3256915}{T_r} + \frac{53.469861915}{T_r^5} +$$

$$\{ 142.50301106 + \frac{2439.3332920}{T_r} - \frac{57.379328503}{T_r^5} \}$$

$$\exp(-\frac{T_r}{10}) + \{ -1.8120154482 + \frac{1.1415112373}{T_r} \}$$

$$\{ 1 - \exp \frac{10}{T_r} \} 10^{-5} \quad (16)$$

$$C^{(1)} = 7122.3669893 - \frac{166472.31956}{T_r} + \frac{2268.6104665}{T_r^5} +$$

$$(9475.01754 + \frac{166222.55809}{T_r} - \frac{2430.7825270}{T_r^5}) \exp(-\frac{T_r}{10})$$

$$+ (-5.5521375772 + \frac{3.3122093147}{T_r})(1 - \exp(\frac{T_r}{10}))10^{-4} \quad (17)$$

$$\begin{aligned} \phi^{(1)} = & -15328.405920 + \frac{1913444.1812}{T_r} - \frac{27377.947640}{T_r^5} \\ & + (-109521.80163 - \frac{1915413.3114}{T_r} + \frac{29342.360092}{T_r^5}) \\ & \exp(-\frac{T_r}{10}) + (0.00713119.38634 - \frac{0.0041948317443}{T_r}) \\ & (1 - \exp \frac{10}{T_r}) \end{aligned} \quad (18)$$

The Third Virial coefficient of CO_2 , n-Butane is calculated using the equation by Chueh⁽³⁰⁾:

$$\begin{aligned} \frac{C}{V_c^2} = & f_c(\frac{T}{T_c}, d) \\ f_c = & (0.332 T_r^{-0.25} + 0.468 T_r^{-5})(1 - e^{(1 - 1.89 T_r^2)}) \\ & -(2.49 - 2.30 T_r + 2.70 T_r^2) \\ & + d \quad (19) \end{aligned}$$

Few values of 'd' given are sufficient to suggest good estimation for other nonpolar gases. By a judicious interpolation, $d = 2$ for n-Butane and $d = 3$ for CO_2 has been chosen.

1.5. Extension to Mixtures

The augmented L.J. equation of state is extended to the binary mixtures of CO_2 and light hydrocarbons upto n-Butane for various compositions at different temperatures.

A significant result of the molecular theory of the Virial equation is the precise composition dependence of the mixture Virial coefficients. Second Virial coefficient is a quadratic function of the mole fraction.

$$B_m = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij} \quad (20)$$

The third Virial coefficient is given by:

$$C_m = \sum_i^m \sum_j^m \sum_k^m y_i y_j y_k C_{ijk} \quad (21)$$

For a binary mixture:

$$B_m = y_1^2 B_1 + 2y_1 y_2 B_{12} + y_2^2 B_2 \quad (22)$$

$$C_m = y_1^3 C_1 + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_2 \quad (23)$$

The equation expresses that mixture Virial coefficients are made up of contributions due to molecular collisions of all sorts, and the weight of given kind is proportional to mole fractions of the components involved. Thus, the coefficients on the right hand side of the equation with indices all referring to the same component are just the Virial coefficients of the pure component. The indices are accordingly abbreviated like B_{11} to B_1 and C_{111} to C_1 etc.

In order to calculate the cross coefficients B_{ij} ($i \neq j$) we specify the parameters v_{cij} , T_{cij} , P_{cij} and ω_{ij} are as follows:

$$v_{cij} = \frac{1}{8} (v_{ci}^{1/3} + v_{cj}^{1/3})^3$$

$$T_{cij} = K_{ij} (T_{ci} T_{cj})^{1/2}$$

where K_{ij} is an adjustable binary parameter.

K_{ij} values are taken from the work of Plocke and Prausnitz⁽³⁴⁾. The interaction third Virial coefficient c_{ijk} is given by:

$$c_{ijk} = (c_{ij} c_{jk} c_{ik})^{1/3} ;$$

$$\text{where } c_{ij} = v_{cij}^2 f_c \left(\frac{T}{T_{cij}} \right), \quad d_{ij}$$

$$d_{ij} = \frac{1}{2} (d_i + d_j)$$

$$c_{112} = (c_{11} c_{13} c_{12})^{1/3}$$

$$c_{122} = (c_{12} c_{22} c_{12})^{1/3}$$

$$\omega_{ij} = \frac{1}{2} (\omega_i + \omega_j)$$

$$z_{cij} = \frac{1}{2} (z_{ci} + z_{cj})$$

In order to find the potential parameter σ_x and ϵ_x for the mixtures, Gubbins⁽²⁵⁾ et al. proposed:

$$\epsilon_x \sigma_x^3 = \sum_{\alpha, \beta} x_\alpha x_\beta \epsilon_{\alpha, \beta} \sigma_{\alpha \beta}^3$$

$$\sigma_x^3 = \sum_{\alpha, \beta} x_\alpha x_\beta \sigma_{\alpha\beta}^3$$

With above mixture rules, the augmented L.J. equation of state for mixtures is written as follows:

$$Z_m^{LJA} = Z_m^{LJ} + (B_{2m} - B_{2m}^{LJ}) \rho + (B_{3m} - B_{3m}^{LJ}) \rho^2 \quad (24)$$

B_{2m} and B_{3m} are real fluid Viral coefficients for the mixture; B_{2m} and B_{3m} are calculated using equations (20) and (21) respectively.

2.4. Calculation of Fugacity Coefficient

The fugacity coefficient is derived from the augmented L.J. equation of state using the relation

$$\ln \phi = \int_{\infty}^V \left(\frac{1}{V} - \frac{P}{RT} \right) dv + Z - 1 - \ln Z \quad (25)$$

resulting in:

$$\begin{aligned} \ln \phi_r &= 2B_2 \rho + \frac{3}{2} B_3 \rho^2 + \frac{4}{3} B_4^{LJ} \rho^3 + \frac{5}{4} B_5^{LJ} \rho^4 + \frac{6}{5} B_6^{LJ} \rho^5 \\ &+ 5 \cdot \frac{1}{6} \cdot B_7^{LJ} \rho^6 - \frac{8}{7} B_8^{LJ} \rho^7 + \frac{23}{27} B_{28}^{LJ} \rho^{27} \\ &+ \frac{30}{29} B_{30}^{LJ} \rho^{29} - \ln Z^{LJA} \end{aligned} \quad (26)$$

The component fugacity coefficient is calculated using the relation:

$$RT \ln \phi_i = \int_{\infty}^V \left\{ \frac{RT}{V} - \left(\frac{P}{n_i T, v, n_j} \right) \right\} dv - RT \ln Z^{LJA} \quad (27)$$

resulting in:

$$\begin{aligned}
 RT \ln \phi_i = & \{ B_{2m}^1 \rho + 2B_{3m}^1 \rho^2 + 3B_{4m}^1 \frac{LJ}{m} \rho^3 + 5B_{6m}^1 \frac{LJ}{m} \rho^5 \\
 & + 30B_{7m}^1 \frac{LJ}{m} \rho^6 - 105B_{8m}^1 \frac{LJ}{m} \rho^7 + 27B_{28}^1 \frac{LJ}{m} \rho^{27} \\
 & + 29B_{30}^1 \frac{LJ}{m} \rho^{29} \} - RT \ln z^{\text{LJA}} \quad (28)
 \end{aligned}$$

This relation can be applied to mixtures with appropriate selection of second and third Virial coefficients for the mixture.

VI. CRITIQUED EQUILIBRIUM CALCULATION

Equation of state is:

$$1 = 1 - \left(B_0 \frac{RT}{v} + A_0 - \frac{C}{T^2} \right) v^2 + \left(\frac{vRT}{T} - a \right) v^3 + a v^6 + \frac{C v^3}{T^2} (1 + v^2) e^{-v^2} \quad (29)$$

Following the suggestion of Statler and Benedict⁽¹⁰⁾ the rule for A_0 has been modified as follows:

$$A_0 = \sum_i x_i^2 A_{oi} + \sum_i \sum_{\substack{j \\ j \neq i \\ j > i}} m_{ij} x_i x_j A_{oi}^{1/2} A_{oj}^{1/2} \quad (30)$$

Whereas in the original equation, m_{ij} is equal to 2, in the modified equation m_{ij} is the value determined from the equilibrium data.

The fugacity of a component in a multicomponent mixture is given by:

$$RT \ln \frac{P_i}{P} = \int_v^\infty \left\{ \left(\frac{\partial \frac{P}{N_i}}{\partial N_i} \right)_{T, V, N_j} - \frac{RT}{V} \right\} dV - RT \ln \frac{V}{N_i RT} \quad (31)$$

3.1. Original Mixing Rules

$$A_0 = \sum_i \sum_j m_{ij} x_i x_j A_{oi}^{1/2} A_{oj}^{1/2} \quad (32)$$

$$B_0 = \sum_i x_i B_{oi} \quad (33)$$

$$c_o = \{ \sum_i (x_i c_{oi}^{1/2}) \}^2 \quad (34)$$

$$b = \{ \sum_i (x_i b_i^{1/3}) \}^3 \quad (35)$$

$$a = \{ \sum_i (x_i a_i^{1/5}) \}^5 \quad (36)$$

$$n = \{ \sum_i (x_i c_i^{1/3}) \}^3 \quad (37)$$

$$s = \{ \sum_i (x_i s_i^{1/3}) \}^3 \quad (38)$$

$$v = \{ \sum_i (x_i v_i^{1/2}) \}^2 \quad (39)$$

3.3. Modified BWR Mixing Rule

$$A_o = \sum_i \sum_j x_i x_j A_{oi}^{1/2} A_{oj}^{1/2} (1 - k_{ij}) \quad (40)$$

The temperature dependence of the C_o coefficients is given in Table I⁽¹²⁾ and C_o has been correlated using the variable $\Delta C_o(T)$, where

$$\Delta C_o^{1/2}(T) = C_o^{1/2}(T_o) - C_o^{1/2}(T)$$

$C_o^{1/2}(T_o)$ is the high temperature value of $C_o^{1/2}$ given in Table I⁽¹²⁾. For temperatures above T_o , C_o is a constant.

For temperatures below T_o , the following equations are used for $\Delta C_o^{1/2}(T)$.

$$\Delta C_o^{1/2}(T) = Q_1 \theta^2 + Q_2 \theta^3 + Q_3 \theta^4 + Q_4 \theta^5$$

where $\theta = \frac{T - T_o}{T_o}$; T is in °R.

using the modified form of mixing rule

$$\begin{aligned}
 \text{RT} \ln \frac{x_i^L}{x_i^V} &= \text{RT} \ln \left(\frac{\rho_i^L}{\rho_i^V} \right) + \{ (B_0 + B_{oi}) \text{RT} - 2(c_0 c_{oi})^{1/2} / T^2 \right. \\
 &\quad \left. + \sum_{j \neq i} x_j (A_{oi} A_{oj})^{1/2} \} \\
 &\quad + \frac{3}{2} \{ (b^2 b_i)^{1/3} \text{RT} - (a^2 a_i)^{1/3} \} r^2 \\
 &\quad + \frac{3}{5} \{ a(a^2 a_i)^{1/3} + a(a^2 a_i)^{1/3} \} r^5 \\
 &\quad + \frac{3 r^2 c}{T^2} (c^2 c_i)^{1/3} \{ \frac{1 - e^{- v_r^2 / v_n^2}}{v_n^2} - \frac{e^{- v_p^2 / 2}}{2} \} \\
 &\quad + \frac{2 r^2 c}{T^2} (\frac{v_i}{v})^{1/2} \{ \frac{1 - e^{- v_p^2 / v_p^2}}{v_p^2} - e^{- v_p^2} \} \\
 &\quad - \frac{v_r^2 e^{- v_r^2 / v_p^2}}{v_p^2} \} \quad (41)
 \end{aligned}$$

where x_i may be either liquid or vapor mole fraction according to whether the density of the liquid or vapor is used.

At equilibrium, fugacities of each component i in all respective phases (V, L) are equal

$$f_i^V = f_i^L \quad \text{and by direct method,}$$

$$f_i^V = \phi_i^V y_i P$$

$$f_i^L = \phi_i^L x_i P$$

$$\text{and vaporisation ratio, } K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V}$$

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A bubble point program^(32,33) was written to satisfy the following conditions for binary systems at a specified temperature and liquid compositions:

$$\psi(d^L, x_1) = \psi(d^V, x_1)$$

$$\beta_1(d^V, x_1) = \beta_1(d^L, x_1)$$

$$\beta_2(d^L, x_2) = \beta_2(d^V, x_2)$$

and

$$x_1 + x_2 = 1.0.$$

In every iteration step, the density of both liquid and vapor is calculated by substitution method of Johnson and Silver⁽¹¹⁾.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Augmented L.J. Equation of State

Compression factors calculated by augmented L.J. equation of state for three types of mixtures at different composition and temperatures studied are shown in Figures 1 to 7. In all the three types of mixtures, it gives reasonably good results upto 1000 psia and at moderate ranges of temperatures (upto 280°F). The deviation get larger for the values of pressures above 1000 psia as seen in Figures 1 and 2.

At high values of temperatures, i.e., above 280°F the results obtained are satisfactory. From the tabulated values, we can conclude that with high percentage of CO₂ in a typical CO₂-hydrocarbon mixture, the equation of state changes its trend from over-prediction to under-prediction.

Since Pope's generalized correlation (18) of third Virial coefficient is based purely on hydrocarbons, at high percentage of CO₂ in the mixture it is not able to give good results with the combination of Lennard-Jones potential. Improvements in the prediction can be made by adopting the equation proposed by Cluech (19) for CO₂-hydrocarbon systems.

Liquid Equilibrium Calculation

The results obtained using bubble pressure program for various systems are tabulated. Application of DWR equation to hot vapor and liquid is restricted by its binary parameter α_{12} . The tabulated Benedict-Webb-Rubin constants (12) are not the best fit values to P-V-T data but are the adjusted parameters improving the generalized correlation for constants in the homologous series.

In this work, binary parameters for calculation are selected approximately so as it can cover the VLE data conditions. It was, therefore, not possible to get accurate values of both bubble pressure and vapor mole fraction.

Values of m_{ij} for certain systems as worked by Crye (12) is taken as such and for the rest of the mixtures it is assumed to be equal to 2, i.e., we adopted the BWR equation with the original mixing rules.

and all the results tabulated are the result above the binary parameter pressure range (by 2 or 3 data points) in order to find the nature of deviation. No definite conclusions can be reached unless proper values of m_{ij} are incorporated in the calculation.

Even though the calculated bubble pressure deviates much from the experimental value, the relative deviation for the equilibrium ratio is found to be smaller as evident from Figures 8 to 13. Figure 9 presents the results of calculation using the proper value of m_{ij} and a marked improvement is evident.

It has been recommended by Chueh and Prausnitz (E&C Standard 6, 492 (1967)) to use the $(1 - k_{ij})$ instead of n_{ij} . However due to the non-availability of the publications mentioned, we could not adopt that. It is felt that with the use of k_{ij} values and the mixing rules proposed by Nakanishi and Saito⁽³⁵⁾ a marked improvement in the results can be achieved.

CHAPTER 5TABULATION OF PARAMETERS USED IN THIS WORKTABLE A: DIFFUSION AND OSMOSIS COEFFICIENTS (E. 12) POTENTIAL⁽³⁾

<u>Molecular Pair</u>	<u>σ Å</u>	<u>$\epsilon / K^{\circ} K$</u>
Methane	3.758	148.6
Ethane	4.443	215.7
Propane	5.118	237.10
Butane	4.687	309.74
CO ₂	3.941	195.2

TABLE B: PURE COMPONENT CONSTANTS USED IN THIS WORK

<u>Substance</u>	<u>T_c (°K)</u>	<u>P_c (atm)</u>	<u>V_c (cm³/gmole)</u>	<u>Z_c</u>	<u>ω</u>
Methane	190.6	45.4	99.0	0.288	0.008
Ethane	205.4	43.2	148.0	0.285	0.098
Propane	360.8	41.9	203.0	0.281	0.152
n-Butane	425.2	37.5	255.0	0.274	0.193
i-Butane	408.1	36.0	263.0	0.283	0.176
n-Pentane	469.6	33.3	304.0	0.262	0.251
n-Hexane	507.4	29.3	370.0	0.260	0.296
CO ₂	304.2	72.8	94.0	0.274	0.225

TABLE C: BINARY INTERACTION PARAMETERS USED IN L.J. POTENTIAL MODEL⁽³⁴⁾

System	<u>K_{ij}</u>
CO ₂ -ethane	0.975
" -ethane	0.938
" -Propene	0.925
" -Isobutane	0.955
" -Isobutane	0.946
" -n-Pentane	1.002
" -n-Hexane	1.018

TABLE D: VALUE OF m_{ij} USED IN THIS WORK FOR VLE CALCULATION

System	<u>m_{ij}</u>
CO ₂ -ethane	1.800
" -Propene	1.766
" -n-Pentane	1.720
" -Isobutane	2.000
" -n-Pentane	1.950
" -n-Hexane	2.000

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CHAPTER 6TABULATION OF RESULTSTABLE 1: EQUIVALENT HARD SPHERE DIAMETER WITH RESPECT TO TEMPERATURE

ETHANE

<u>Temperature, °F</u>	<u>Hard Sphere Dia, Å</u>
100.0000	4.3656797
160.0000	4.3602681
220.0000	4.3551331
280.0000	4.3502445
340.0000	4.3455775
400.0000	4.3411108
460.0000	4.3368262

PROPANE

40.0000	5.0407505
100.0000	5.0344579
160.0000	5.0284986
220.0000	5.0228348
280.0000	5.0174352
340.0000	5.0122735
400.0000	5.0073275
460.0000	5.0025780

Contd....

TABLE 1 (continued)

N-BUTANE

<u>Temperature, °F</u>	<u>Hard Sphere Dia, Å</u>
100.0000	4.6447068
160.0000	4.6412199
220.0000	4.6378599
280.0000	4.6346162
340.0000	4.6314797
400.0000	4.6284422
460.0000	4.6254967

CARBON DIOXIDE

40.0000	3.8730368
100.0000	3.8677112
160.0000	3.8626859
220.0000	3.8579253
280.0000	3.8533999
340.0000	3.8490855
400.0000	3.8449614
460.0000	3.8410099

COMPRESSIBILITY FACTOR (USLM, ADJUSTED) - REFERENCE TABLES
 POTENTIAL FOR CO₂ (LAWTON AND 2) - STATION

TEMP. F	4M expt 1	ZML 1	ZML 2 advfr	ZML 3 advfr	ZML 4 advfr
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Y1= 0.2000

PRESSURE= 200.0PSIA

160.000	.9439	.9594	.9372	.9403	-0.379
220.000	.9571	.9704	.9546	.9567	-0.013
280.000	.9680	.9790	.9668	.9681	0.015
340.000	.9762	.9853	.9754	.9764	0.015
400.000	.9822	.9900	.9818	.9825	0.026
460.000	.9871	.9936	.9865	.9876	-0.007

Y1= 0.2000

PRESSURE= 400.0PSIA

160.000	.8820	.9095	.8640	.8785	-0.399
220.000	.9128	.9373	.9041	.9131	0.035
280.000	.9360	.9563	.9309	.9368	0.083
340.000	.9529	.9698	.9496	.9535	0.065
400.000	.9652	.9797	.9630	.9657	0.056
460.000	.9749	.9871	.9729	.9749	-0.001

Y1= 0.2000

PRESSURE= 600.0PSIA

160.000	.8158	.8514	.7775	.8157	-0.013
220.000	.8673	.9001	.8478	.8703	0.344
280.000	.9046	.9319	.8925	.9066	0.226
340.000	.9297	.9536	.9225	.9319	0.233
400.000	.9486	.9692	.9437	.9502	0.164
460.000	.9630	.9808	.9592	.9638	0.078

$\gamma_1 = 0.2000$

PRESSURE= 600.0Psia

160.000	.7395	.7804	.6717	.7543	1.035
220.000	.8217	.8592	.7456	.8301	1.912
280.000	.8730	.9051	.8517	.8706	2.613
340.000	.9077	.9371	.8940	.9120	3.475
400.000	.9329	.9588	.9212	.9301	4.339
460.000	.9522	.9746	.9455	.9539	5.176

 $\gamma_1 = 0.2000$

PRESSURE=1000.0Psia

160.000	.6598	.6958	.5435	.7055	5.934
220.000	.7705	.8151	.7176	.7955	9.499
280.000	.8438	.8790	.8093	.8593	1.291
340.000	.8817	.9205	.8663	.8948	0.796
400.000	.9184	.9487	.9048	.9239	0.597
460.000	.9419	.9689	.9321	.9455	0.360

 $\gamma_1 = 0.2000$

PRESSURE=1250.0Psia

160.000	.5708	.5879	.3680	.7062	23.716
220.000	.7245	.7589	.6284	.7682	6.030
280.000	.8093	.8467	.7551	.8315	2.746
340.000	.8645	.9008	.8311	.8780	1.560
400.000	.9023	.9370	.8811	.9120	1.080
460.000	.9306	.9627	.9161	.9375	0.742

 $\gamma_1 = 0.2000$

PRESSURE=1500.0Psia

160.000	.5088	.5347	.2386	.8515	67.364
220.000	.6794	.7093	.5423	.7712	13.509
280.000	.7795	.8169	.7027	.8214	5.374
340.000	.8440	.8830	.7973	.8682	2.870
400.000	.8882	.9269	.8588	.9048	1.866
460.000	.9208	.9578	.9013	.9328	1.301

T1 = 1.2000

PRESSURE=1500.0PSIA

100.000	.4897	.5612	.2253	1.1259	129.019
220.000	.6103	.6793	.4244	.8157	25.573
280.000	.7501	.7939	.6566	.3252	9.539
340.000	.8273	.8689	.7669	.6674	4.841
400.000	.8773	.9193	.8388	.9030	2.936
460.000	.9134	.9548	.8983	.9318	2.017

T1 = 0.2000

PRESSURE=2000.0PSIA

100.000	.4971	.6967	.2926	1.4342	153.518
220.000	.6279	.6802	.4393	.9157	45.831
280.000	.7390	.7815	.6209	.8556	15.775
340.000	.8159	.8601	.7420	.8708	7.465
400.000	.8684	.9149	.8220	.9075	4.505
460.000	.9075	.9539	.8775	.9351	3.039

T1 = 0.2000

PRESSURE=2250.0PSIA

100.000	.5183	.8263	.3903	1.7193	231.722
220.000	.6246	.7133	.4408	1.0501	68.131
280.000	.7279	.7830	.5996	.9057	24.425
340.000	.8080	.8579	.7237	.8977	11.106
400.000	.8631	.9145	.8093	.9189	6.464
460.000	.9043	.9558	.8695	.9429	4.264

Aver. Abs. Deviation, % = 15.5759

COMPRESSIBILITY FACTOR USING AUGERED THERMOPHYSICAL PROPERTIES
POTENTIAL FUNCTION CO2(1)-ETHYLIC(2) MIXTURE

TEMP F	ZMIX,1	ZMIX,2	ZMIX,3	ZMIX,4
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Y1= 0.6000

PRESSURE= 200.0PsiA

100.000	.9370	.9611	.9277	.9301	-0.734
160.000	.9542	.9735	.9499	.9515	-0.274
220.000	.9661	.9821	.9645	.9657	-0.039
280.000	.9749	.9882	.9746	.9754	0.055
340.000	.9814	.9926	.9817	.9823	0.044
400.000	.9865	.9959	.9868	.9873	0.085
460.000	.9905	.9983	.9907	.9911	0.057

Y1= 0.6000

PRESSURE= 400.0PsiA

100.000	.8645	.9142	.8418	.8537	-1.294
160.000	.9060	.9436	.8939	.9010	-0.548
220.000	.9315	.9626	.9262	.9313	-0.022
280.000	.9500	.9757	.9478	.9515	0.155
340.000	.9635	.9850	.9628	.9655	0.205
400.000	.9735	.9918	.9735	.9755	0.209
460.000	.9812	.9968	.9814	.9829	0.178

Y1= 0.6000

PRESSURE= 600.0PsiA

100.000	.7794	.8554	.7350	.7669	-1.608
160.000	.8543	.9097	.8306	.8487	-0.661
220.000	.8960	.9416	.8848	.8972	-0.132

280.000	.9246	.9626	.9197	.9284	0.416
340.000	.9158	.9773	.9434	.9497	0.416
400.000	.9606	.9878	.9601	.9649	0.433
460.000	.9725	.9956	.9723	.9758	0.336

Y1= 0.6000

PRESSURE= 800.0Psia

100.000	.6785	.7779	.5935	.6682	-1.518
160.000	.7997	.8713	.7587	.7953	-0.554
220.000	.8604	.9192	.8404	.8642	0.445
280.000	.9000	.9493	.8904	.9069	0.771
340.000	.9284	.9698	.9237	.9354	0.754
400.000	.9488	.9842	.9467	.9553	0.681
460.000	.9643	.9947	.9633	.9697	0.556

Y1= 0.6000

PRESSURE=1000.0Psia

100.000	.5575	.6714	.3904	.5637	1.117
160.000	.7422	.8284	.6766	.7431	0.116
220.000	.8257	.8959	.7933	.8337	0.974
280.000	.8767	.9361	.8605	.8877	1.250
340.000	.9122	.9626	.9039	.9229	1.173
400.000	.9373	.9810	.9336	.9472	1.059
460.000	.9563	.9942	.9547	.9648	0.884

Y1= 0.6000

PRESSURE=1250.0Psia

100.000	.3852	.5660	.0585	.6243	52.066
160.000	.6697	.7712	.5610	.6885	2.810
220.000	.7830	.8667	.7315	.8010	2.396
280.000	.8487	.9202	.8226	.8679	2.260
340.000	.8935	.9544	.8796	.9105	1.903
400.000	.9242	.9778	.9177	.9396	1.671
460.000	.9476	.9944	.9445	.9606	1.367

Y1= 0.6000

PRESSURE=1500.0Psia

100.000	.3449	.7992	.1191	1.1353	229.164
160.000	.6031	.7227	.4427	.6690	10.927
220.000	.7444	.8404	.6696	.7816	5.004
280.000	.8240	.9063	.7857	.8548	3.743
340.000	.8767	.9478	.8563	.9025	2.946
400.000	.9126	.9759	.9028	.9353	2.482
460.000	.9400	.9957	.9353	.9588	1.995

Y1= 0.6000

PRESSURE=1750.0Psia

100.000	.3621	1.0498	.2940	1.5489	327.747
160.000	.5529	.7108	.3544	.7210	30.397
220.000	.7113	.8213	.6128	.7798	9.628
280.000	.8024	.8958	.7513	.8506	5.007
340.000	.8621	.9434	.8348	.8990	4.387
400.000	.9035	.9756	.8895	.9345	3.434
460.000	.9333	.9982	.9273	.9596	2.921

Y1= 0.6000

PRESSURE=2000.0Psia

100.000	.3899	1.2626	.4604	1.8740	380.640
160.000	.5278	.7582	.3315	.8569	62.349
220.000	.6849	.8150	.5675	.8028	17.209
280.000	.7843	.8905	.7216	.8573	9.308
340.000	.8494	.9420	.8160	.9036	5.383
400.000	.8953	.9773	.8780	.9379	4.759
460.000	.9280	1.0022	.9207	.9634	3.818

Aver. Abs. Deviation, % = 19.3561

COMPRESSIBILITY FACTOR USING AUGMENTED LENNARD-JONES
 POTENTIAL FOR CO₂(1)-ETHANE(2) MIXTURE

TEMP F	ZMext1	ZMLJ	ZMLJA 2ndVir	ZMLJA 3rdVir	%DEVIATION ZMLJA
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Y1 = 0.8000

PRESSURE = 200.0PSIA

160.000	.9562	.9770	.9334	.9345	-2.267
220.000	.9680	.9846	.9532	.9541	-1.435
280.000	.9774	.9900	.9667	.9675	-1.015
340.000	.9833	.9940	.9762	.9769	-0.655
400.000	.9880	.9969	.9831	.9837	-0.440
460.000	.9917	.9991	.9883	.9887	-0.304

Y1 = 0.8000

PRESSURE = 400.0PSIA

160.000	.9108	.9512	.8598	.8645	-5.080
220.000	.9358	.9690	.9029	.9070	-3.080
280.000	.9543	.9796	.9318	.9351	-2.011
340.000	.9670	.9878	.9517	.9544	-1.302
400.000	.9766	.9938	.9660	.9682	-0.865
460.000	.9835	.9983	.9765	.9782	-0.538

Y1 = 0.8000

PRESSURE = 600.0PSIA

160.000	.8623	.9222	.7773	.7893	-8.464
220.000	.9022	.9592	.8490	.8587	-4.821
280.000	.9311	.9688	.8953	.9031	-3.002
340.000	.9508	.9817	.9266	.9329	-1.887
400.000	.9651	.9909	.9488	.9536	-1.167
460.000	.9756	.9978	.9649	.9687	-0.709

$\chi_1 = 0.8000$

PRESSURE = 800.0 Psia

160.000	.8123	.8898	.6848	.7088	-12.746
220.000	.8686	.9313	.7911	.8098	-6.769
280.000	.9085	.9578	.8573	.8720	-4.014
340.000	.9343	.9756	.9010	.9124	-2.341
400.000	.9534	.9883	.9314	.9403	-1.377
460.000	.9681	.9976	.9533	.9602	-0.813

$\chi_1 = 0.8000$

PRESSURE = 1000.0 Psia

160.000	.7576	.8535	.5787	.6218	-17.927
220.000	.8361	.9117	.7297	.7612	-8.957
280.000	.8858	.9468	.8180	.8422	-4.927
340.000	.9189	.9699	.8750	.8935	-2.762
400.000	.9431	.9851	.9141	.9283	-1.569
460.000	.9609	.9977	.9420	.9530	-0.827

$\chi_1 = 0.8000$

PRESSURE = 1250.0 Psia

160.000	.6883	.8045	.4264	.5080	-26.192
220.000	.7960	.8870	.6480	.7024	-11.759
280.000	.8588	.9335	.7675	.8077	-5.953
340.000	.9002	.9634	.8423	.8725	-3.080
400.000	.9305	.9840	.8928	.9156	-1.605
460.000	.9524	.9985	.9283	.9457	-0.703

$\chi_1 = 0.8000$

PRESSURE = 1500.0 Psia

160.000	.6203	.7585	.2550	.3997	-35.556
220.000	.7568	.8630	.5621	.6488	-14.272
280.000	.8335	.9217	.7164	.7778	-6.681

340.000	.8833	.9582	.8100	.8551	-3.187
400.000	.9193	.9829	.8722	.9057	-1.478
460.000	.9448	1.0003	.9153	.9407	-0.429

$\chi_1 = 0.8000$

PRESSURE=1750.0Psia

160.000	.5597	.7357	.0847	.3266	-41.639
220.000	.7214	.8454	.4762	.6060	-15.997
280.000	.8108	.9124	.6662	.7545	-6.943
340.000	.8678	.9546	.7787	.8423	-2.936
400.000	.9087	.9831	.8524	.8992	-1.050
460.000	.9380	1.0030	.9032	.9383	0.034

$\chi_1 = 0.8000$

PRESSURE=2000.0Psia

160.000	.5221	.7654	-.0321	.3310	-36.596
220.000	.6909	.8363	.3957	.5805	-15.973
280.000	.7914	.9070	.6187	.7398	-6.522
340.000	.8541	.9534	.7491	.8349	-2.246
400.000	.8992	.9849	.8340	.8964	-0.316
460.000	.9318	1.0070	.8921	.9387	0.736

$\chi_1 = 0.8000$

PRESSURE=2250.0Psia

160.000	.5068	.8524	-.0719	.4158	-17.952
220.000	.6684	.8414	.3291	.5790	-13.371
280.000	.7746	.9069	.5756	.7356	-5.040
340.000	.8429	.9552	.7223	.8338	-1.083
400.000	.8918	.9887	.8175	.8977	0.665
460.000	.9264	1.0124	.8824	.9420	1.684

$\chi_1 = 0.8000$

PRESSURE=2500.0Psia

160.000	.5082	.9741	-.0501	.5488	7.987
220.000	.6522	.8649	.2814	.6056	-7.150

280.000	.7621	.9137	.5395	.7435	-2.437
340.000	.8343	.9605	.6991	.8395	0.627
400.000	.8853	.9947	.8031	.9036	2.072
460.000	.9227	1.0194	.8744	.9485	2.797

$X_1 = 0.8000$

PRESSURE=2750.0Psia

160.000	.5194	1.1097	.0074	.7011	34.979
220.000	.6447	.9071	.2579	.6593	2.261
280.000	.7531	.9285	.5120	.7648	1.551
340.000	.8280	.9698	.6801	.8527	2.981
400.000	.8811	1.0032	.7915	.9143	3.766
460.000	.9200	1.0281	.8681	.9583	4.168

$Y_1 = 0.8000$

PRESSURE=3000.0Psia

160.000	.5373	1.2421	.0796	.8511	58.101
220.000	.6445	.9658	.2573	.7353	14.090
280.000	.7487	.9517	.4947	.7991	6.725
340.000	.8236	.9839	.6661	.8737	6.079
400.000	.8792	1.0144	.7829	.9297	6.741
460.000	.9192	1.0386	.8639	.9715	5.687

Aver. Abs. Deviation, % = 7.1189

COMPRESSIBILITY FACTOR USING AUGMENTED TENNARD-JONES
 POTENTIAL FOR CO₂(1)-PROPANE(2) MIXTURE

TEMP F	Z _M exptl	Z _M LJ	Z _M TJA 2ndVir	Z _M TJA 3rdVir	%DEVIATION Z _M LJ
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220.000	.9123	.9544	.9129	.9183	0.654
280.000	.9348	.9681	.9361	.9396	0.514
340.000	.9508	.9778	.9522	.9545	0.391
400.000	.9616	.9849	.9637	.9653	0.385
460.000	.9711	.9903	.9723	.9731	0.236

 Y₁ = 0.2000

PRESSURE = 200.0 Psia

220.000	.9123	.9544	.9129	.9183	0.654
280.000	.9348	.9681	.9361	.9396	0.514
340.000	.9508	.9778	.9522	.9545	0.391
400.000	.9616	.9849	.9637	.9653	0.385
460.000	.9711	.9903	.9723	.9731	0.236

 Y₁ = 0.2000

PRESSURE = 800.0 Psia

220.000	.5305	.7071	.4218	.6744	27.125
280.000	.7120	.8373	.6696	.7656	7.530
340.000	.7985	.8986	.7767	.8294	3.865

400,000	.8514	.9363	.8405	.8729	2.526
460,000	.8986	.9621	.8834	.9044	1.783

Y1= 0.2000

PRESSURE=1000.0Psia

220,000	.4162	.6893	.2347	.8758	110.439
280,000	.6347	.7915	.5563	.7451	17.392
340,000	.7485	.8731	.7105	.8042	7.440
400,000	.8180	.9224	.7978	.8526	4.229
460,000	.8659	.9553	.8543	.8890	2.670

Y1= 0.2000

PRESSURE=1250.0Psia

220,000	.3715	1.0693	.4327	1.6900	354.925
280,000	.5695	.7783	.4507	.8170	43.467
340,000	.6944	.8538	.6348	.8048	15.904
400,000	.7805	.9115	.7483	.8424	7.925
460,000	.8410	.9512	.8213	.8787	4.484

Aver.Abs.Deviation.%= 30.6941

COMPRESSIBILITY FACTOR USING AUGMENTED LENNARD JONES
 POTENTIAL FOR CO₂(1)-PROPANE(2) MIXTURE

TEMP F	ZM _{exptl}	ZMLJA	ZMLJA 2ndVir	ZMLJA 3rdVir	%DEVIATION ZMLJA
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Y₁ = 0.4000

PRESSURE = 200.0 psia

160.000	.9069	.9498	.9189	.9242	1.907
220.000	.9349	.9646	.9423	.9458	1.165
280.000	.9508	.9754	.9577	.9601	0.974
340.000	.9635	.9832	.9686	.9702	0.691
400.000	.9715	.9889	.9764	.9775	0.615
460.000	.9789	.9932	.9822	.9830	0.416

Y₁ = 0.4000

PRESSURE = 800.0 psia

160.000	.7998	.7628	.6270	.7360	-7.981
220.000	.6976	.8110	.6915	.7914	13.445
280.000	.7945	.8837	.7993	.8529	7.346
340.000	.8544	.9265	.8607	.8931	4.531
400.000	.8912	.9545	.8999	.9210	3.346
460.000	.9198	.9743	.9273	.9416	2.367

Y1 = 0.4000

PRESSURE=1000.0 Psia

160.000	.6658	.6586	.4546	.7004	5.201
220.000	.6165	.7489	.5799	.7797	26.480
280.000	.7445	.8509	.7383	.8336	11.965
340.000	.8195	.9079	.8222	.8773	7.051
400.000	.8669	.9444	.8742	.9091	4.873
460.000	.9025	.9697	.9098	.9330	3.376

Y1 = 0.4000

PRESSURE=1250.0 Psia

160.000	.4850	.5915	.2414	.9652	99.012
220.000	.5195	.7122	.4615	.9014	73.508
280.000	.6883	.8179	.6656	.8398	22.012
340.000	.7800	.8890	.7764	.8714	11.723
400.000	.8408	.9349	.8445	.9025	7.336
460.000	.8850	.9664	.8900	.9276	4.910

Aver. Abs. Deviation, % = 13.4224

COMPRESSIBILITY FACTOR USING AUGMENTED LENNARD-JONES
 POTENTIAL FOR CO₂(1)-PROPANE(2) MIXTURE

TEMP F	ZMeyer1	ZMLJ	ZMLJA 2ndVir	ZMLJA 3rdVir	%DEVIATION ZMLJA
160					
Y1 = 0.8000					
PRESSURE = 200.0 psia					
160.000	.9485	.9715	.9296	.9313	+1.818
220.000	.9638	.9807	.9506	.9519	+1.234
280.000	.9735	.9871	.9648	.9658	+0.789
340.000	.9800	.9918	.9748	.9756	+0.451
400.000	.9853	.9953	.9820	.9927	+0.269
460.000	.9995	.9979	.9874	.9979	+0.163
160					
Y1 = 0.8000					
PRESSURE = 400.0 psia					
160.000	.8920	.9387	.8496	.8569	+3.930
220.000	.9253	.9595	.8968	.9025	+2.463
280.000	.9468	.9735	.9275	.9320	+1.565
340.000	.9610	.9834	.9496	.9521	+0.930
400.000	.9709	.9906	.9637	.9663	+0.472
460.000	.9799	.9960	.9747	.9769	+0.317
160					
Y1 = 0.8000					
PRESSURE = 600.0 psia					
160.000	.8301	.9004	.7569	.7759	+6.528
220.000	.8860	.9364	.8382	.8522	+3.812
280.000	.9190	.9592	.8881	.8988	+2.196
340.000	.9419	.9749	.9216	.9297	+1.790
400.000	.9574	.9861	.9451	.9512	+0.643
460.000	.9698	.9944	.9621	.9668	+0.306

Y1 = 0.8000

PRESSURE = 800.0 Psia

160,000	.7635	.8558	.6477	.6876	-0.938
220,000	.8439	.9113	.7738	.8014	-5.037
280,000	.8925	.9445	.8469	.8671	-2.844
340,000	.9231	.9665	.8940	.9090	-1.524
400,000	.9439	.9819	.9264	.9377	-0.660
460,000	.9597	.9932	.9497	.9582	-0.157

Y1 = 0.8000

PRESSURE = 1000.0 Psia

160,000	.6910	.8038	.5165	.5926	-14.237
220,000	.8022	.8849	.7042	.7518	-6.283
280,000	.8639	.9296	.8036	.8373	-3.083
340,000	.9045	.9594	.8660	.8904	-1.560
400,000	.9310	.9792	.9078	.9259	-0.540
460,000	.9500	.9924	.9374	.9511	0.111

Y1 = 0.8000

PRESSURE = 1250.0 Psia

160,000	.5976	.7345	.3192	.4783	-19.968
220,000	.7484	.8514	.6091	.6947	-7.181
280,000	.8270	.9116	.7470	.8043	-2.730
340,000	.8870	.9495	.8316	.8713	-1.771
400,000	.9164	.9744	.8851	.9147	-0.236
460,000	.9385	.9923	.9228	.9446	0.645

Y1 = 0.8000

PRESSURE = 1500.0 Psia

160,000	.5076	.6956	.1089	.4265	-15.987
220,000	.6982	.8219	.5104	.6519	-6.633
280,000	.7938	.8960	.6902	.7799	-1.755
340,000	.8587	.9418	.7957	.8567	-0.238
400,000	.9010	.9721	.8631	.9065	0.610
460,000	.9279	.9934	.9090	.9411	1.426

Y1 = 0.8000

160,000	.4534	.7756	.0092	.5510	21.523
220,000	.6548	.8054	.4178	.6368	-2.751
280,000	.7648	.8853	.6362	.7676	0.368
340,000	.8388	.9372	.7627	.8497	1.295
400,000	.8874	.9718	.8426	.9035	1.819
460,000	.9200	.9960	.8967	.9412	2.303

Y1 = 0.8000

PRESSURE=2000.0 Psia.

160,000	.4421	.9601	.0618	.8061	82.336
220,000	.6213	.8134	.3465	.6642	6.910
280,000	.7433	.8825	.5896	.7713	2.770
340,000	.8227	.9365	.7333	.8513	3.478
400,000	.8752	.9740	.8243	.9061	3.535
460,000	.9135	1.0004	.8862	.9450	3.452

Aver. Abs. Deviation.% = 4.9608

COMPRESSIBILITY FACTOR USING THE CLOUD DENNARD JONES
POTENTIAL FOR CO₂(1)-N₂O₄(2) MIXTURE

TEMP F	ZMext1	ZMLJ	ZMLJA 2ndVir	ZMLJA 3rdVir	%DEVIATION ZMLJA
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$\chi_1 = 0.2000$

PRESSURE= 200.0PsiA

340.000	.9160	.9848	.9213	.9257	1.057
400.000	.9360	.9903	.9401	.9431	0.763
460.000	.9514	.9944	.9537	.9559	0.476

$\chi_1 = 0.2000$

PRESSURE= 400.0PsiA

340.000	.8235	.9662	.8256	.8459	2.831
400.000	.8685	.9795	.8711	.8854	1.944
460.000	.8991	.9886	.9025	.9123	1.465

$\chi_1 = 0.2000$

PRESSURE= 600.0PsiA

340.000	.7188	.9432	.7005	.7650	6.423
400.000	.7988	.9676	.7909	.8288	3.757
460.000	.8487	.9829	.8460	.8707	2.596

$\chi_1 = 0.2000$

PRESSURE= 800.0PsiA

340.000	.6052	.9161	.5318	.6933	14.563
400.000	.7288	.9555	.6973	.7783	6.792
460.000	.7985	.9779	.7839	.8335	4.387

$\chi_1 = 0.2000$

PRESSURE= 1000.0PsiA

340.000	.4955	.8961	.3094	.6860	38.444
400.000	.6620	.9457	.5904	.7438	12.361
460.000	.7538	.9747	.7178	.8049	5.778

Aver. Abs. Deviation.% = 6.9759

COMPRESSIBILITY FACTOR USING AUGMENTED TERNARY LINES

POTENTIAL FOR CH₂(1)-C₂H₅AK(2)-ITAF₂(3)

TEMP F	ZMext1	ZM ₂ T	ZM ₂ AK 2ndVir	ZM ₂ AK 3rdVir	SPREADING Z ₄ TA
$\gamma_1 = 0.5000$					
PRESSURE= 200.0Psi _a					
340.000	.9528	.9894	.9620	.9648	1.1.1
400.000	.9640	.9936	.9714	.9724	0.913
460.000	.9728	.9958	.9783	.9793	0.669
$\gamma_1 = 0.5000$					
PRESSURE= 400.0Psi _a					
340.000	.9040	.9778	.9200	.9241	2.781
400.000	.9290	.9870	.9408	.9470	1.937
460.000	.9451	.9936	.9555	.9599	1.576
$\gamma_1 = 0.5000$					
PRESSURE= 600.0Psi _a					
340.000	.8560	.9653	.8738	.8907	4.756
400.000	.8935	.9802	.9092	.9233	3.338
460.000	.9195	.9908	.9320	.9425	2.499
$\gamma_1 = 0.5000$					
PRESSURE= 800.0Psi _a					
340.000	.8060	.9522	.8226	.8686	7.766
400.000	.8572	.9737	.8736	.9028	5.319
460.000	.8935	.9884	.9078	.9275	3.900
$\gamma_1 = 0.5000$					
PRESSURE= 1000.0Psi _a					
340.000	.7580	.9394	.7671	.8484	11.928
400.000	.8245	.9679	.8378	.8871	7.598
460.000	.8700	.9868	.8833	.9157	5.257
$\gamma_1 = 0.5000$					
PRESSURE= 1250.0Psi _a					
340.000	.7030	.9264	.6941	.8418	19.761

400,000	.7875	.9628	.7425	.8770	11,370
460,000	.8435	.9864	.8531	.9070	7,522

$\chi_1 = 0.5000$

PRESSURE = 1500.0 psia

340,000	.6610	.9216	.6252	.8659	30,981
400,000	.7572	.9617	.7492	.9049	15,329
460,000	.8220	.9887	.8246	.9062	10,243

Aver. Abs. deviation, $\chi_1 = 7.5004$

COMPRESSIBILITY FACTOR USING AUGUSTINOFF'S LAW AND THERMOPOTENTIAL FOR $CO_2(1) + CH_4(2) + X^3CO_2$

TEMP F	Z _{Meptl}	Z _{Mlt}	Z _{1,01} 2ndvir	Z _{1,01} 3rdvir	%DEVIATION Z _{1,01}
$\chi_1 = 0.7000$					
PRESSURE= 200.0PsiA					
340,000	.9691	.9920	.9724	.9735	0.455
400,000	.9770	.9955	.9798	.9806	0.372
460,000	.9820	.9981	.9854	.9859	0.390
$\chi_1 = 0.7000$					
PRESSURE= 400.0PsiA					
340,000	.9375	.9835	.9430	.9479	1.164
400,000	.9541	.9909	.9589	.9622	0.852
460,000	.9648	.9963	.9704	.9722	0.825
$\chi_1 = 0.7000$					
PRESSURE= 600.0PsiA					
340,000	.9068	.9748	.9119	.9236	1.866
400,000	.9314	.9864	.9373	.9451	1.473
460,000	.9479	.9948	.9553	.9608	1.356

$\chi_1 = 0.7000$

PRESSURE= 600.0PsiA

340,000	.8750	.9660	.8791	.9014	3.0120
400,000	.9090	.9822	.9151	.9237	2.270
460,000	.9326	.9937	.9401	.9502	1.865

$\chi_1 = 0.7000$

PRESSURE=1000.0PsiA

340,000	.8458	.9575	.8451	.8825	4.2325
400,000	.8885	.9785	.8927	.9146	3.163
460,000	.9171	.9932	.9250	.9413	2.636

$\chi_1 = 0.7000$

PRESSURE=1250.0PsiA

340,000	.8106	.9480	.8015	.8650	6.710
400,000	.8650	.9750	.8644	.9043	4.539
460,000	.9015	.9935	.9068	.9331	3.505

$\chi_1 = 0.7000$

PRESSURE=1500.0PsiA

340,000	.7806	.9413	.7587	.8573	9.823
400,000	.8438	.9734	.8378	.8975	6.367
460,000	.8864	.9952	.8895	.9286	4.763

Aver. Abs. Deviation, % = 2.9390

SYSTEM: CO2(1)-METHANE(2)

TEMP: -65.000F,

PRESS: 10. PSIA

SLNO.	PRESS	EXPERIMENTAL VALUES,		CALCULATED VALUES,		% DEVIATIONS	
		X(1)	Y(1)	AK(1)	Y(1)	Pealc	DELP
1	300.000	.9150	.3000	0.3279	.2941	0.3214	319.704
2	400.000	.8730	.2430	0.2784	.2492	0.2855	402.130
3	573.000	.7280	.1860	0.2555	.2000	0.2747	580.111
4	600.000	.7440	.1950	0.2621	.2035	0.2736	564.885
5	700.000	.7200	.1850	0.2569	.2075	0.2882	582.570

Aver. Abs. Deviations, % :

ADEP= 6.1939

ADEK1= 5.7151

SYSTEM: CO2(1)-METHANE(2)

TEMP: =57.0000F;

PRESS: IN PSIA

SLNO.	PRESS	EXPERIMENTAL		CALCULATED		VALUES, % DEVIATIONS		DELK(1)
		X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	
1	300.000	.9300	.3450	0.3710	.3611	0.3883	306.650	2.217 4.677
2	400.000	.8900	.2770	0.3112	.2955	0.3321	395.861	-1.035 6.695
3	573.000	.7590	.2130	0.2806	.2268	0.2988	587.557	2.540 6.484
4	600.000	.8470	.2430	0.2869	.2650	0.3129	472.063	-21.323 9.054
5	700.000	.8320	.3590	0.4315	.2595	0.3119	492.620	-29.626 -27.718

Aver. Abs. Deviations, % :

ADEP= 11.3481

ADEK1= 10.9255

SYSTEM: CO2(1)-METHANE(2)
 TEMP: -25.0000F; PRESS: 7N PSIA

SLNO.	PRESS	EXPERIMENTAL		VALUES, CALCULATED		VALUES, CALCULATED		% DEVIATIONS	
		X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	300.000	1.0000	1.0000	1.0000	1.0000	1.0000	195.156	-34.948	0.000
2	400.000	.9370	.5210	0.5560	.5314	0.5672	397.576	-0.606	2.005
3	573.000	.8430	.3600	0.4270	.3795	0.4502	609.844	6.430	5.415
4	600.000	.8690	.3890	0.4465	.4037	0.4645	561.281	-6.453	4.036
5	700.000	.8320	.3590	0.4315	.3724	0.4476	629.732	-10.038	3.743

Aver. Abs. Deviations, % :

ADEP= 11.6951

ADEK1= 3.0399

SYSTEM: CO2(1)-PROPANE(2)

TEMP: -40.000F;

PRESS:1N PSIA

		EXPERIMENTAL		VALUES,		CALCULATED		VALUES,		% DEVIATIONS	
SI.NO.	PRESS	X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)

1	15.000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	15.803	5.351	0.000
2	50.000	.1650	.7100	.43000	.6950	.42123	.49.865	.-0.270	-2.040		
3	100.000	.5280	.8820	1.6700	.8829	1.6722	102.769	2.769	0.129		
4	145.000	1.0000	1.0000	1.0000	1.0000	1.0000	146.355	0.935	0.000		

Aver. Abs. Deviations, % :

ADEP= 2.3310

ADEK1= 0.5423

SYSTEM: CO₂(1)-PROPANE(2)
 TEMP: -4.0000F;
 PRESS: IN PSIA

SLNO.	PRSS	EXPERIMENTAL		VALUES,		CALCULATED		VALUES,		% DEVIATIONS	
		X(1)	Y(1)	AK(1)	Y(1)	AK(1)	AK(1)	Pcalc	DELP	DELK(1)	
1	34.000	.0000	.0000	0.0000	0.0000	0.0000	34.960	34.960	2.823	0.000	
2	100.000	.1900	.6560	3.4500	6.762	3.5590	98.460	98.460	-1.540	3.161	
3	200.000	.5180	.8510	1.6400	.8613	1.6627	185.088	185.088	-7.456	1.385	
4	250.000	.8200	.9280	1.1300	.9357	1.1411	249.213	249.213	-0.315	0.986	
5	285.000	1.0000	1.0000	1.0000	1.0000	1.0000	285.117	285.117	0.041	0.000	

Aver. Abs. Deviations, % :

ADFP = 2.4349
 ADEK1 = 1.1063

SYSTEM: CO2(1)-PROPANE(2)

TEMP: 11.8000F;

PRESS: TN PSIA

SLNO.	PRESS	EXPERIMENTAL		CALCULATED		VALUES, % DEVIATIONS		DELK(1)
		X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	
1	35.280	.0000	.0000	.0000	.0000	.0000	47.690	35.176 0.000
2	48.510	.0300	.3130	10.4330	.2235	.4498	61.177	26.112 -28.594
3	66.150	.0550	.5130	9.3270	.3442	.2573	72.044	8.910 -32.912
4	91.140	.1250	.6610	5.2880	.5438	.3502	100.509	10.280 -17.735
5	113.190	.1770	.7230	4.0850	.6278	.5468	120.573	6.523 -13.174
6	141.120	.2460	.7760	3.1540	.7021	.8541	145.593	3.170 -9.510
7	163.170	.3220	.8110	2.5190	.7571	.3514	171.799	5.288 -6.655
8	188.160	.4010	.8450	2.1070	.7982	.9905	197.559	4.995 -5.531
9	214.620	.5440	.8780	1.6140	.8514	.5651	241.525	12.536 -3.033
10	241.080	.6940	.9060	1.3050	.8939	.2880	285.145	18.278 -1.305
11	266.070	.8680	.9510	1.0960	.9432	.0866	335.197	25.981 -0.857
12	283.710	1.0000	1.0000	1.0000	1.0000	0.000	370.574	30.617 0.000

Aver. Abs. Deviations, % :

ADEP= 15.6554

ADEK1= 9.9421

SYSTEM: CO2(1)-PROPANE(2)

TEMP: 32.0000F; PRFSS:TN PSIA

EXPERIMENTAL VALUES, CALCULATED VALUES, % DEVIATIONS

SLNO.	PRESS	X(1)	AK(1)	Y(1)	AK(1)	Y(1)	Pcalc	DELP	DELK(1)
1	67.000	.0000	.0000	.0000	.0000	.0000	69.018	3.013	0.000
2	100.000	.0550	.3300	.6.000	.3127	.5.6852	97.483	-2.517	-5.247
3	200.000	.2600	.6830	.2.6300	.6872	.2.6429	194.384	-2.808	0.490
4	300.000	.4800	.8180	.1.7000	.8131	.1.6940	285.964	-4.679	-0.352
5	400.000	.7120	.8820	.1.2400	.8899	.1.2484	381.175	-4.706	0.680
6	507.000	1.0000	1.0000	1.0000	1.0000	1.0000	504.869	-0.420	0.000

Aver. Abs. Deviations, % :

ADEP= 3.0238

ADEK1= 1.1282

SYSTEM: CO2(1)-PROPANE(2)

TEMP: 32.0000F;

PRESS: IN PSIA

EXPERIMENTAL

VALUES,
X(1) Y(1) AK(1)

SLNo. PRESS Y(1) AK(1) Y(1) AK(1) Pcalc DEUP DELK(1)

SLNo.	PRESS	X(1)	AK(1)	Y(1)	AK(1)	Pcalc	DEUP	DELK(1)
1	69.90	.0000	.0000	.0000	.0000	69.018	-0.104	0.000
2	80.850	.0130	.1270	10.0450	.0967	7.4375	75.937	-6.076
3	107.310	.0340	.3300	9.6660	.2187	6.4329	87.093	-18.840
4	149.940	.0860	.5230	6.1460	.4149	4.8249	113.773	-24.121
5	216.090	.1760	.6740	3.8290	.5944	3.3770	156.621	-27.521
6	277.830	.2910	.7450	2.5630	.7116	2.4455	207.657	-25.258
7	358.680	.4610	.8280	1.7960	.8050	1.7462	278.691	-22.301
8	402.780	.6220	.8590	1.3820	.8614	1.3849	343.864	-14.627
9	438.060	.7190	.8930	1.2420	.8907	1.2388	383.883	-12.367
10	470.400	.8400	.9290	1.1050	.9288	1.1057	436.233	-7.263
11	498.330	.9530	.9760	1.0250	.9744	1.0225	485.613	-2.552
12	505.680	1.0000	1.0000	1.0000	1.0000	504.869	-0.160	0.000

Aver. Abs. Deviations, % :

ADEP= 13.4325

ADEK1= 8.4033

SYSTEM: CO₂(1)-PROPANE(2)

TEMP: 40.0000F;

PRESS:IN PSIA

EXPERIMENTAL

VALUES, CALCULATED VALUES, % DEVIATIONS

SLNO.	PRESS	X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	79.000	.0000	.0000	.0000	.0000	.0000	78.731	-0.340	0.000
2	100.000	.0247	.2056	.8.3200	.1607	.6.5049	93.061	-6.939	-21.816
3	150.000	.0884	.4676	.5.2900	.4071	.4.6051	128.385	-14.410	-12.948
4	200.000	.1602	.6036	.3.7700	.5562	.3.4722	165.334	-17.333	-7.900
5	250.000	.2402	.6864	.2.8580	.6551	.2.7273	204.517	-18.193	-4.575
6	300.000	.3316	.7431	.2.2410	.7277	.2.1944	247.064	-17.645	-2.080
7	350.000	.4361	.7876	.1.8060	.7841	.1.7979	294.523	-15.850	-0.446
8	400.000	.5532	.8309	.1.5020	.8307	.1.5017	347.175	-13.206	-0.020
9	450.000	.6714	.8688	.1.2940	.8697	.1.2953	402.059	-10.654	0.099
10	500.000	.7956	.9102	.1.1440	.9095	.1.1432	462.985	-7.403	-0.070
11	550.000	.9401	.9702	.1.0320	.9669	.1.0285	537.313	-2.307	-0.338
12	566.500	1.0000	1.0000	1.0000	1.0000	1.0000	566.326	-0.031	0.000

Aver. Abs. Deviations, % :

ADFP= 10.3593

ADEK1= 4.1910

SYSTEM: CO₂(1)-PROPANE(2)

TEMP: 70.0000F;

PRESS: IN PSIA

FXPERIMENTAL

VALUES,

AK(1) Y(1) AK(1) Y(1) AK(1) VALUES, % DEVIATIONS

SLNO. PRESS X(1) Y(1) AK(1) Y(1) AK(1) Pcalc DELP DELK(1)

1	125.000	.0000	.0000	.0000	.0000	125.862	0.690	0.000
2	150.000	.0245	.1618	.6.6000	.1312	5.3538	143.574	-4.284
3	200.000	.0742	.3589	4.8400	.3137	4.2284	178.443	-10.778
4	250.000	.1274	.4812	3.7800	.4402	3.4556	213.797	-14.481
5	300.000	.1834	.5634	3.0700	.5319	2.9000	249.459	-16.847
6	350.000	.2423	.6235	2.5730	.6014	2.4820	286.329	-18.192
7	400.000	.3048	.6718	2.2040	.6567	2.1547	323.412	-19.147
8	450.000	.3727	.7148	1.9180	.7033	1.8870	363.798	-19.156
9	500.000	.4443	.7518	1.6920	.7419	1.6698	407.267	-18.547
10	550.000	.5178	.7814	1.5090	.7761	1.4989	452.361	-17.753
11	600.000	.5937	.8092	1.3630	.8062	1.3579	502.764	-16.206
12	650.000	.6722	.8368	1.2450	.8356	1.2430	558.849	-14.023
13	700.000	.7516	.8673	1.1550	.7516	1.0000	350.317	-49.955
14	750.000	.8275	.9011	1.0890	.8275	1.0000	379.657	-49.379
15	800.000	.9046	.9417	1.0410	.9045	0.9999	411.906	-48.512
16	850.000	.9805	.9874	1.0070	.9805	1.0000	449.573	-47.109
17	860.900	1.0000	1.0000	1.0000	1.0000	1.0000	462.397	-46.289

Aver. Abs. Deviations, % :

ADEP= 24.1969

ADEK1= 4.8109

SYSTEM: CO2(1)-PROPANE(2)

TEMP: 100.0000F; PRESS: IN PSIA

EXPERIMENTAL VALUES, CALCULATED VALUES, % DEVIATIONS

SLNo.	PRESS	X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	188.700	.0000	.0000	.0000	.0000	.0000	189.847	0.608	0.000
2	200.000	.0081	.0472	5.8300	.0382	4.7166	197.530	-1.235	-19.098
3	250.000	.0495	.2281	4.6100	.1951	3.9421	232.017	-7.193	-14.487
4	300.000	.0926	.3511	3.7900	.3114	3.3628	267.562	-10.813	-11.271
5	350.000	.1361	.4370	3.2100	.3989	2.9310	300.731	-14.077	-8.690
6	400.000	.1799	.4994	2.7760	.4667	2.5943	333.979	-16.505	-6.546
7	450.000	.2248	.5481	2.4390	.5222	2.3229	366.584	-18.537	-4.758
8	500.000	.2709	.5876	2.1690	.5685	2.0987	399.293	-20.141	-3.242
9	550.000	.3191	.6213	1.9470	.6083	1.9062	433.421	-21.196	-2.093
10	600.000	.3693	.6514	1.7640	.6429	1.7410	468.961	-21.840	-1.304
11	650.000	.4212	.6781	1.6100	.6734	1.5987	506.296	-22.108	-0.702
12	700.000	.4735	.7013	1.4810	.6995	1.4772	545.215	-22.112	-0.255
13	750.000	.5272	.7238	1.3730	.5268	0.9992	356.918	-52.411	-27.228
14	800.000	.5814	.7448	1.2810	.5814	1.0000	376.982	-52.877	-21.938
15	850.000	.6346	.7647	1.2050	.6346	1.0000	394.335	-53.608	-17.014
16	900.000	.6861	.7801	1.1370	.6861	1.0000	413.543	-54.051	-12.051
17	950.000	.7363	.7908	1.0740	.7363	1.0000	431.102	-54.621	-6.894
18	1000.000	.7902	.7973	1.0090	.7902	1.0000	453.052	-54.695	-0.893
19	1002.500	.7950	1.0000	.7948	0.9997	454.117	-54.702	-0.027	

Aver. Abs. Deviations, % :

SYSTEM: CO₂(1)-PROPANE(2)
 TEMP: 130.000F; PRESS: 111 PSIA

EXPERIMENTAL VALUES, CALCULATED VALUES, % DEVIATIONS
 SINO. PRESS X(1) AK(1) Y(1) AK(1) PCALC DELP DELK(1)

SINO.	PRESS	X(1)	AK(1)	Y(1)	AK(1)	PCALC	DELP	DELK(1)
1	237.500	.0000	.0000	0.0000	.0000	275.351	15.937	0.000
2	300.000	.0176	.0734	4.1700	.0636	292.608	-2.464	-13.291
3	350.000	.0526	.1873	3.5600	.1679	3.1918	325.481	-7.005
4	400.000	.0882	.2739	3.1000	.2519	2.8563	356.516	-10.344
5	450.000	.1246	.3425	2.7490	.3206	2.5731	388.118	-13.752
6	500.000	.1618	.3980	2.4600	.3784	2.3390	418.423	-16.315
7	550.000	.1992	.4476	2.2220	.4265	2.1412	448.546	-18.446
8	600.000	.2376	.4804	2.0220	.4680	1.9698	478.224	-20.296
9	650.000	.2770	.5024	1.8500	.5033	1.8170	508.063	-21.836
10	700.000	.3171	.5394	1.7010	.3168	0.9990	416.921	-40.440
11	750.000	.3577	.5619	1.5710	.3577	0.9999	388.423	-48.210
12	800.000	.3996	.5806	1.4530	.3996	1.0000	401.450	-49.819
13	850.000	.4403	.5896	1.3390	.4403	1.0000	414.519	-51.233
14	900.000	.4840	.5968	1.2330	.4840	1.0000	428.303	-52.411
15	950.000	.4306	.5980	1.1270	.4306	1.0000	411.316	-56.704
16	992.000	.4880	.5880	1.0000	.4880	1.0000	428.954	-56.759

Aver. Abs. Deviations, % :

ADEP = 30.1561
 ADEK1 = 13.4438

TEMP: 32.000F; PRFSS: IN PSIA

SL.NO.	PRFSS	X(1)	Y(1)	EXPERIMENTAL			CALCULATED			VALUES, % DEVIATIONS		
				AK(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)	
1	35.280	.0300	.5880	19.6000	.5292	17.6389	31.256	.41.407		-10.006		
2	57.330	.0570	.7410	13.0000	.6715	11.7816	45.950	-19.850		-9.373		
3	85.260	.0940	.8260	8.7872	.7616	8.1020	65.499	-23.177		-7.797		
4	122.010	.1440	.8770	6.0903	.8234	5.7178	90.226	-26.050		-6.117		
5	155.820	.2000	.9000	4.5000	.8604	4.3021	115.905	-25.616		-4.397		
6	189.630	.2750	.9160	3.3309	.8902	3.2369	149.531	-21.146		-2.822		
7	224.910	.3340	.9200	2.7545	.9042	2.7071	174.634	-22.354		-1.719		
8	261.660	.3980	.9320	2.3417	.9155	2.3002	201.257	-23.085		-1.773		
9	294.000	.4690	.9420	2.0085	.9250	1.9723	231.148	-21.378		-1.803		
10	336.630	.5680	.9510	1.6743	.9365	1.6488	273.248	-18.828		-1.523		
11	377.790	.6810	.9630	1.4141	.9481	1.3923	324.058	-14.223		-1.542		
12	420.420	.8040	.9740	1.2145	.9614	1.1958	386.833	-7.989		-1.538		
13	463.050	.9110	.9830	1.0790	.9778	1.0733	448.125	-3.223		-0.527		

Aver. Abs. Deviations, % :

ADEP = 18.3328

ADEK1 = 3.9182

SYSTEM: CU2(1)-N-BUTANE(2)

TEMP: 69.7800F; PRESS: IN PSIA

EXPERIMENTAL		VALUES, CALCULATED		VALUES, % DEVIATIONS					
SLNO.	PRESS	X(1)	Y(1)	AK(1)	PCalc	DELP	DELK(1)		
1	59.976	.0066	.1320	20.0000	.1409	21.3525	36.200	-39.643	6.763
2	79.968	.0220	.3320	15.0909	.3532	16.0562	47.756	-40.281	6.397
3	100.107	.0360	.4540	12.6111	.4722	13.1178	57.856	-42.206	4.017
4	125.097	.0560	.5560	9.9286	.5816	10.3856	72.109	-42.357	4.603
5	150.087	.0760	.6280	8.2632	.6520	8.5793	86.588	-42.308	3.826
6	175.077	.0950	.6790	7.1474	.6999	7.3675	99.632	-43.092	3.080
7	200.067	.1151	.7140	6.2033	.7379	6.4109	113.189	-43.424	3.347
8	238.434	.1550	.7650	4.9355	.7906	5.1010	138.672	-41.840	3.353
9	300.027	.1950	.7980	4.0923	.8255	4.2336	163.149	-45.622	3.452
10	350.154	.2390	.8220	3.4393	.8522	3.5658	189.202	-45.966	3.678
11	408.954	.2840	.8400	2.9577	.8727	3.0730	214.076	-47.653	3.898
12	450.114	.3300	.8550	2.5909	.8880	2.6908	239.925	-46.697	3.856
13	500.094	.3780	.8670	2.2937	.9003	2.3818	266.698	-46.670	3.844
14	600.201	.4780	.8860	1.8536	.9197	1.9240	321.702	-46.401	3.803
15	700.161	.5840	.9000	1.5411	.9339	1.5992	384.865	-45.032	3.770
16	800.268	.6980	.9100	1.3037	.9462	1.3556	462.694	-42.183	3.980
17	900.228	.7860	.9250	1.1768	.7854	0.9993	86.323	-90.411	-15.090
18	1000.335	.8710	.9440	1.0838	.8707	0.9996	89.698	-91.033	-7.769
19	1005.627	.0980	.9490	9.6837	.7062	7.2059	101.742	-89.883	-25.587
20	1057.224	.9400	.9400	1.0000	.9398	0.9998	87.615	-91.713	-0.016

Aver. Abs. Deviations, % :

ADEP= 53.2208

SYSTEM: CO2(1)-N-BUTANE(2)

TEMP: 100.0000F;

PRESS: 1N PSIA

S.I.NO.	PRESS	EXPERIMENTAL		CALCULATED		VALUES,		% DEVIATIONS	
		X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	51.500	.0000	.0000	.0000	.0000	.0000	53.460	3.807	0.000
2	100.000	.0340	.4540	12.4900	.3801	11.1785	83.112	-16.888	-10.500
3	200.000	.1150	.7140	6.2100	.6712	5.8369	150.940	-24.530	-6.009
4	300.000	.1960	.7980	4.0700	.7729	3.9431	211.872	-29.376	-3.117
5	400.000	.2840	.8400	2.9600	.8298	2.9219	272.237	-31.941	-1.286
6	500.000	.3780	.8670	2.2940	.8647	2.2876	333.750	-33.250	-0.280
7	600.000	.4780	.8860	1.8520	.8883	1.8584	400.910	-33.182	0.347
8	700.000	.5840	.9000	1.5400	.9060	1.5514	479.284	-31.531	0.740
9	800.000	.6890	.9100	1.3210	.6890	1.0000	294.917	-63.135	-24.302
10	900.000	.7860	.9250	1.1770	.7860	1.0000	356.461	-60.393	-15.040
11	1000.000	.8710	.9440	1.0840	.8707	0.9997	419.860	-58.014	-7.778
12	1095.000	.9400	.9400	1.0000	.9400	1.0000	487.792	-55.453	-0.000

Aver. Abs. Deviations, % :

ADEP= 36.7916

ADEK1= 5.7832

SYSTEM: C02(1)-ISOBUTANE(2)

TEMP: 32.0000F; PRESS:101 PSIA

EXPERIMENTAL VALUES, CALCULATED VALUES, % DEVIATIONS

ST.NO.	PRESS	X(1)	Y(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	22.785	.0000	.0000	.0000	.0000	.0000	21.962	-3.613	0.000
2	39.600	.0220	.4220	19.1820	.3567	16.2135	35.581	-10.354	-15.475
3	51.450	.0370	.5410	14.6220	.4810	13.0011	44.127	-14.233	-11.085
4	61.740	.0380	.6230	16.3950	.4868	12.8116	44.867	-27.329	-21.856
5	74.970	.0530	.6900	13.0190	.5684	10.7249	53.221	-29.010	-17.621
6	91.140	.0730	.7440	10.1920	.6423	8.7990	64.449	-29.286	-13.667
7	108.790	.0980	.7830	7.0900	.7040	7.1836	78.293	-28.027	-10.092
8	123.480	.1400	.8000	5.3600	.7788	5.2270	105.558	-14.514	-2.645
9	144.060	.1660	.8300	5.0000	.7956	4.7978	114.302	-20.657	-4.145
10	171.990	.2240	.8630	3.8530	.8354	3.7293	143.927	-16.317	-3.211
11	214.620	.3170	.9770	2.7670	.8725	2.7524	187.935	-12.434	-0.529
12	242.550	.3780	.8990	2.3780	.8869	2.3462	216.351	-10.801	-1.336
13	255.720	.4030	.9130	2.2660	.9920	2.2133	227.335	-11.121	-2.324
14	266.070	.4160	.9140	2.1970	.9947	2.1506	232.729	-12.531	-2.110
15	310.170	.5130	.9220	1.7970	.9081	1.7702	276.268	-10.930	-1.491

Aver. Abs. Deviations, % :

ADFP# 16.7438

ADEK1= 7.1726

SYSTEM: CO₂(1)-N-PENTANE(2)
 TEMP: 40,1000F; PRESS:IN PSIA

EXPERIMENTAL VALUES, CALCULATED VALUES, % DEVIATIONS
 SLNO: PRESS X(1) AK(1) Y(1) AK(1) Pcalc DELP DELK(1)

SLNO:	PRESS	X(1)	AK(1)	Y(1)	AK(1)	Pcalc	DELP	DELK(1)
1	4.300	.0000	.0000	.0000	.0000	4.247	-1.225	0.000
2	33.000	.0290	.8528	29.4070	.7510	25.8955	21.364	-35.262
3	82.000	.0856	.9449	11.0390	.8790	10.2682	51.757	-36.881
4	160.000	.1834	.9709	5.2940	.9236	5.0362	100.632	-37.105
5	247.000	.3179	.9803	3.0840	.9422	2.9638	161.850	-34.474
6	325.000	.4858	.9846	2.0270	.9490	1.9535	238.416	-26.641
7	397.000	.6255	.9872	1.5780	.9494	1.5179	306.717	-22.741
8	471.000	.8229	.9874	1.2020	.9593	1.1657	438.180	-6.968

Aver. Abs. Deviations, % :

ADEP= 25.1622
 ADEK1= 4.7676

SYSTEM: CO2(1)-N-HEXANE(2)

TEMP: 112.0000F;

PRESS:IN PSIA

EXPERIMENTAL

VALUES,

SLNO. PRESS X(1) Y(1) AK(1) Y(1) AK(1) Pcalc DELP DELK(1)

1	113.000	.0800	.9490	11.8625	.9251	11.5635	84.978	-24.798
2	240.000	.1700	.9720	5.7176	.9566	5.6271	158.897	-33.793
3	354.000	.2520	.9770	3.8770	.9762	3.8740	269.691	-23.816
4	480.000	.3560	.9820	2.7584	.9767	2.7435	334.731	-30.264
5	600.000	.4500	.9820	2.1822	.9871	2.1935	449.646	-25.059
6	733.000	.5740	.9840	1.7143	.9999	1.7421	5.731	-99.218
7	844.000	.6870	.9850	1.4338	.9919	1.4438	690.547	-18.182
8	973.000	.8290	.9840	1.1870	.8286	0.9995	268.977	-72.356
9	1039.000	.8820	.9820	1.1134	.8817	0.9997	349.777	-66.335
10	1085.000	.9150	.9810	1.0721	.9147	0.9997	406.176	-62.564

Aver. Abs. Deviations, % :

ADEP= 45.6386

ADEK1= 4.0324

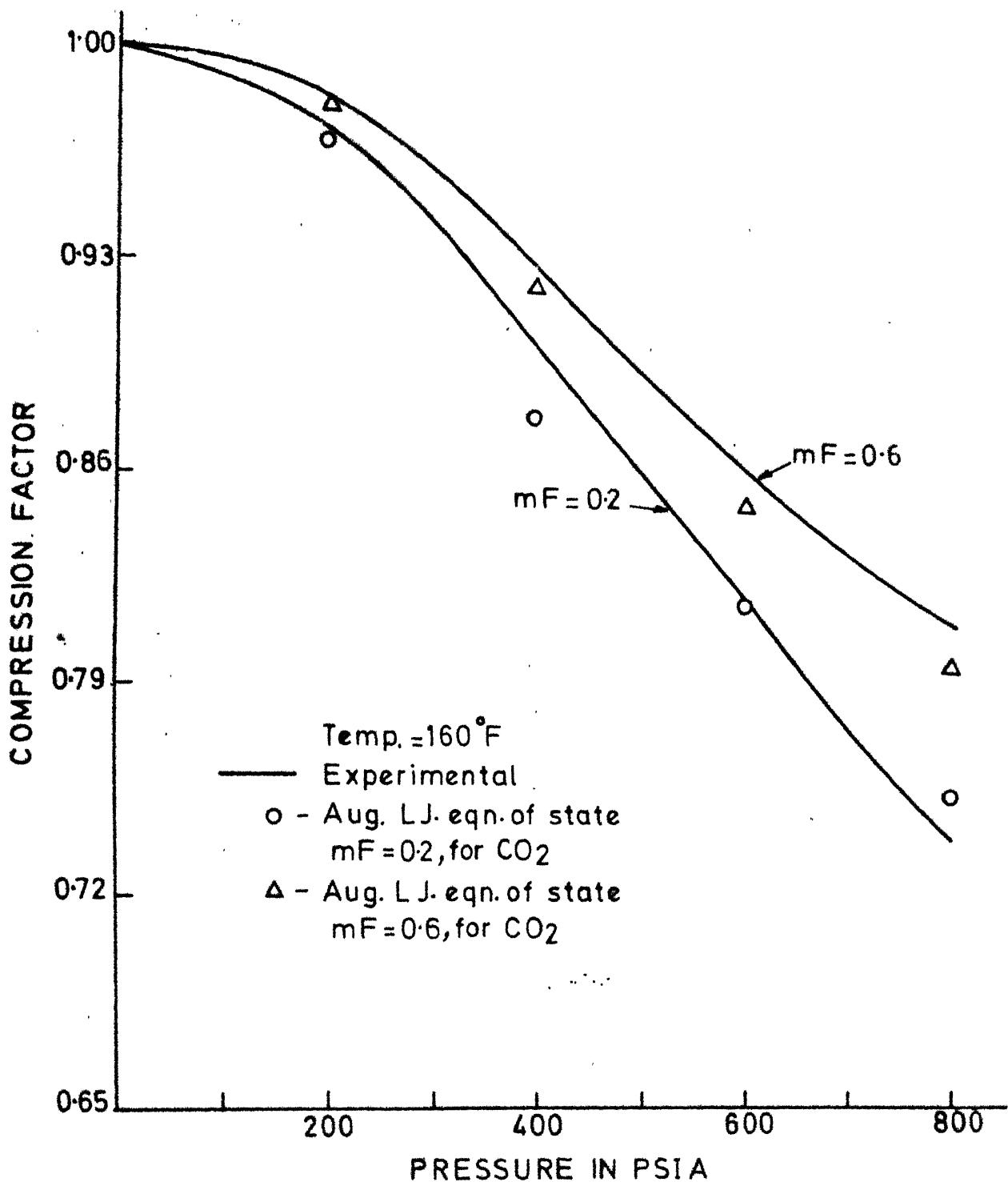


FIG. 1 COMPRESSION FACTOR OF CARBONDIOXIDE - ETHANE-MIXTURE

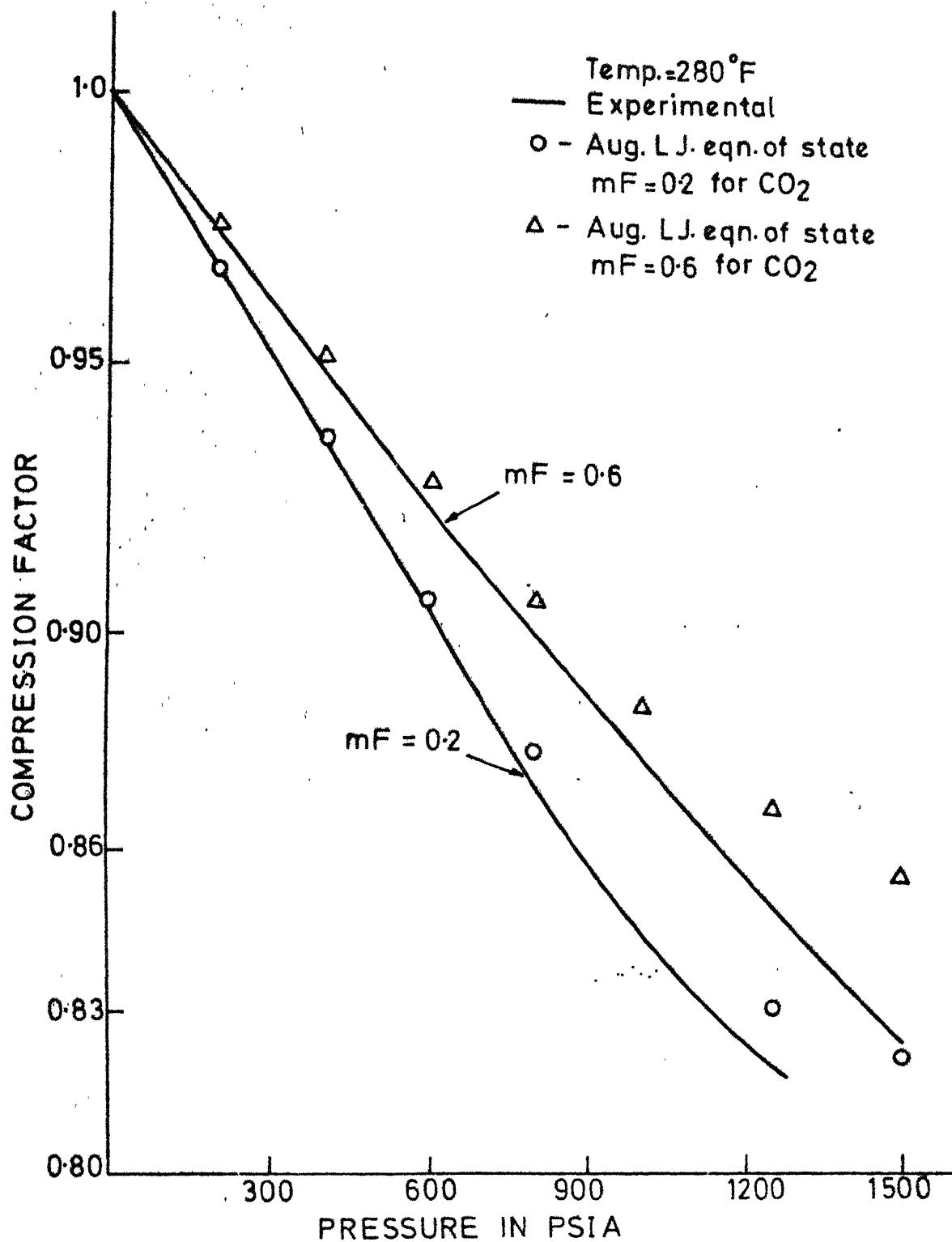


FIG. 2 COMPRESSION FACTOR OF CARBON DIOXIDE
 ETHANE-MIXTURE

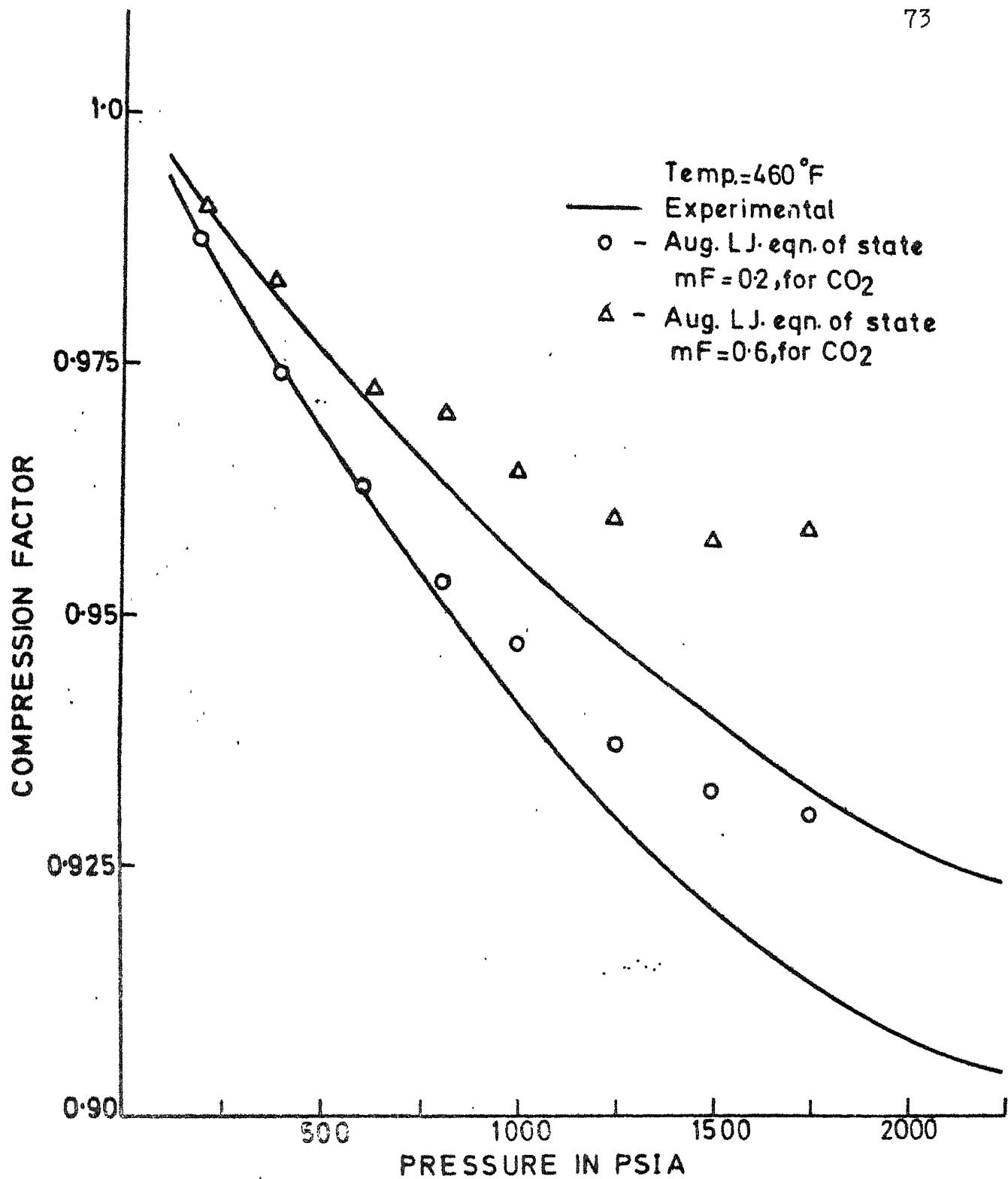


FIG. 3 COMPRESSION FACTOR OF CARBON DIOXIDE-ETHANE MIXTURE

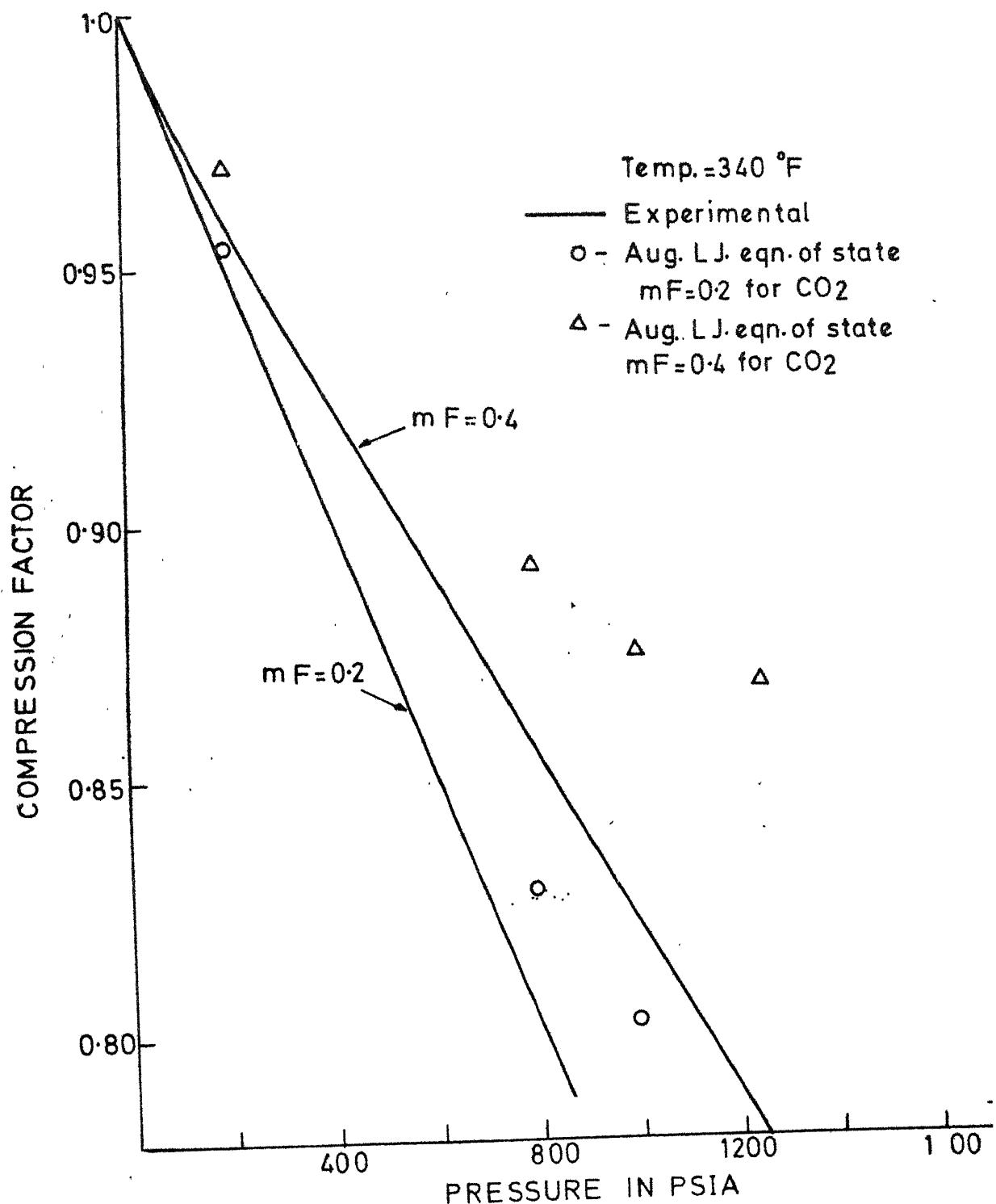


FIG. 4 COMPRESSION FACTOR OF CARBON DIOXIDE PROPROPANE MIXTURES

COMPRESSION FACTOR

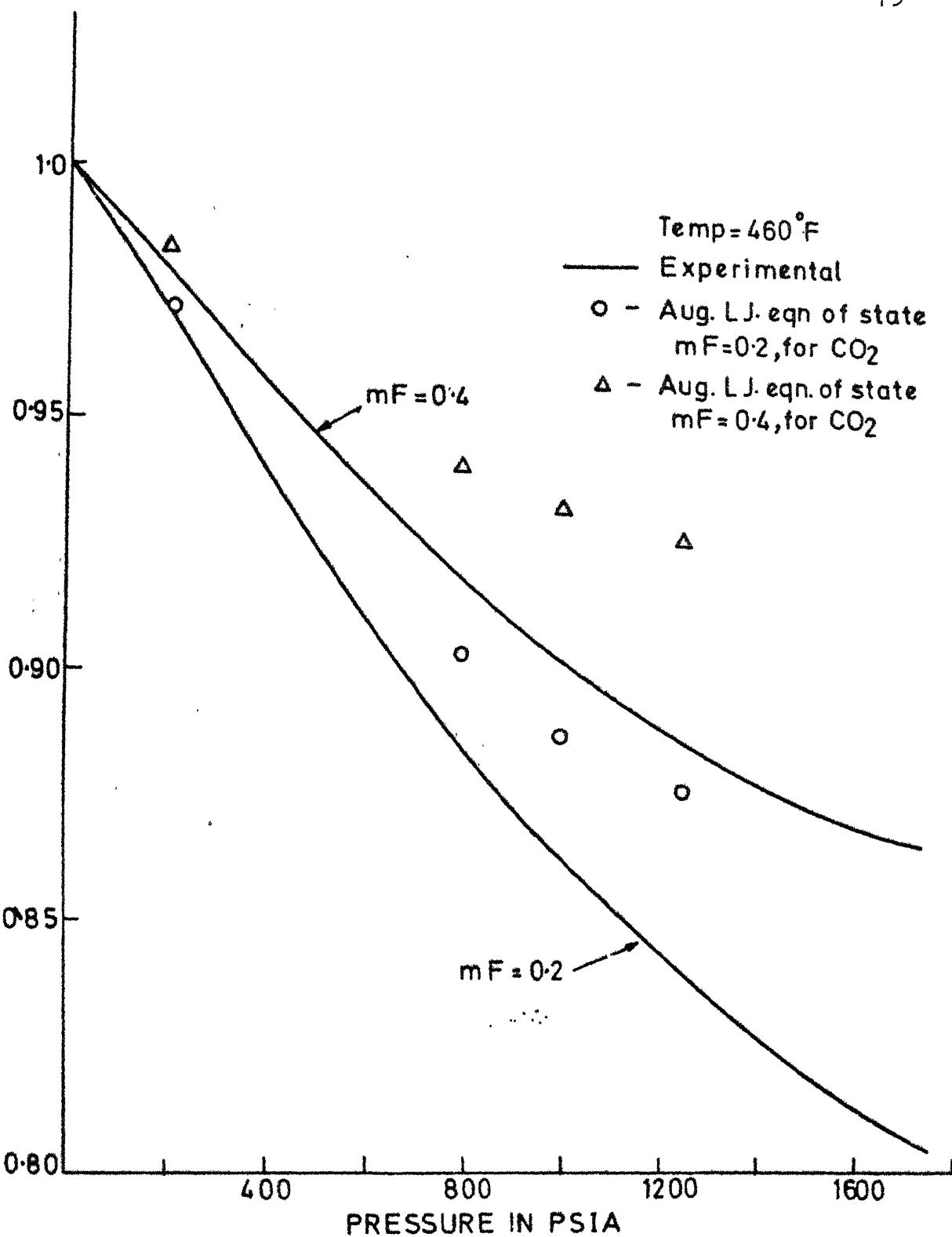


FIG. 5 COMPRESSION FACTOR OF CARBONDIOXIDE-PROPANE MIXTURES

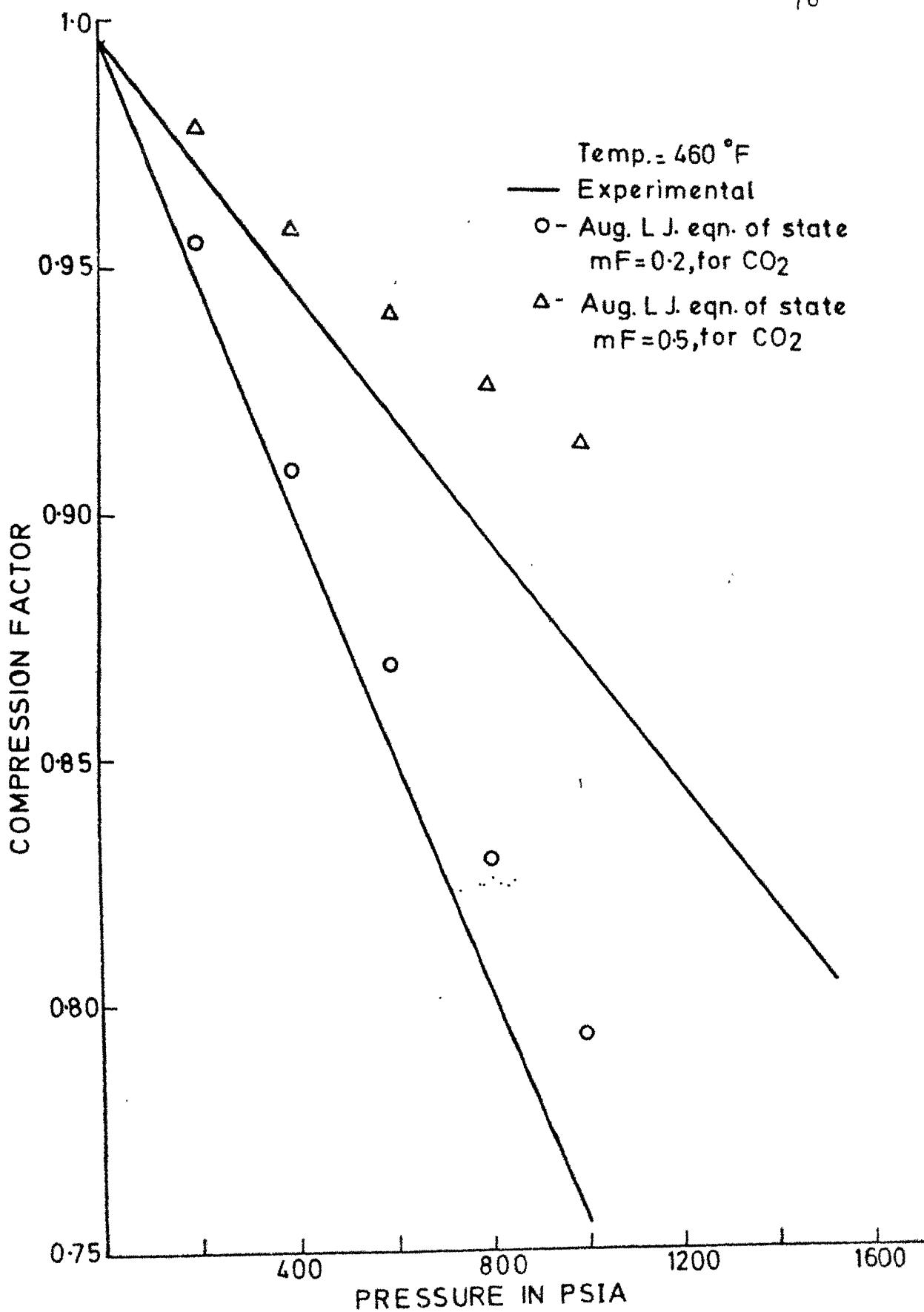


FIG. 6 COMPRESSION FACTOR OF CARBONDIOXIDE n BUTANE MIXTURE

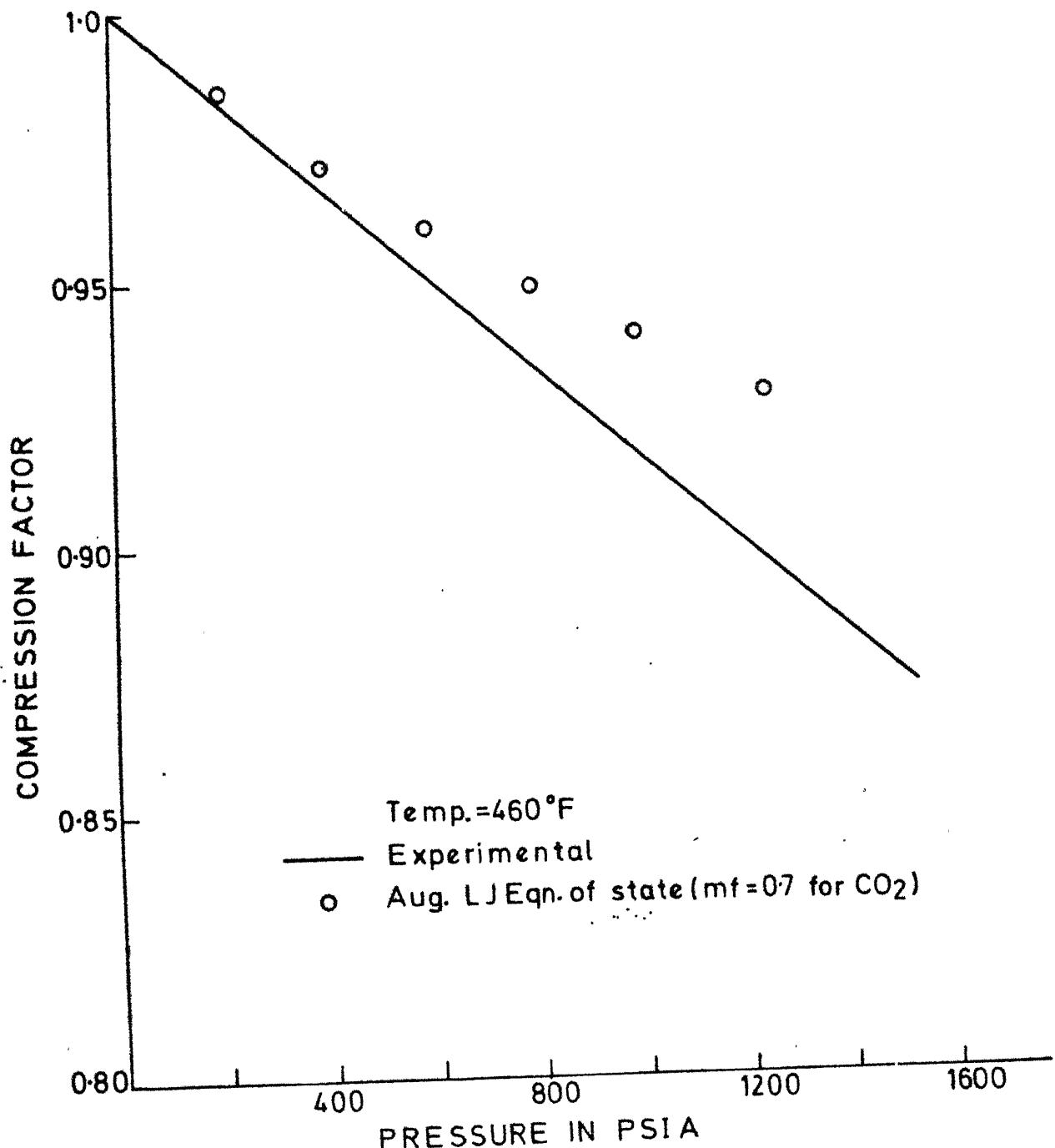


FIG. 7 COMPRESSION FACTOR OF CARBONDIOXIDE-
n-BUJANE MIXTURE

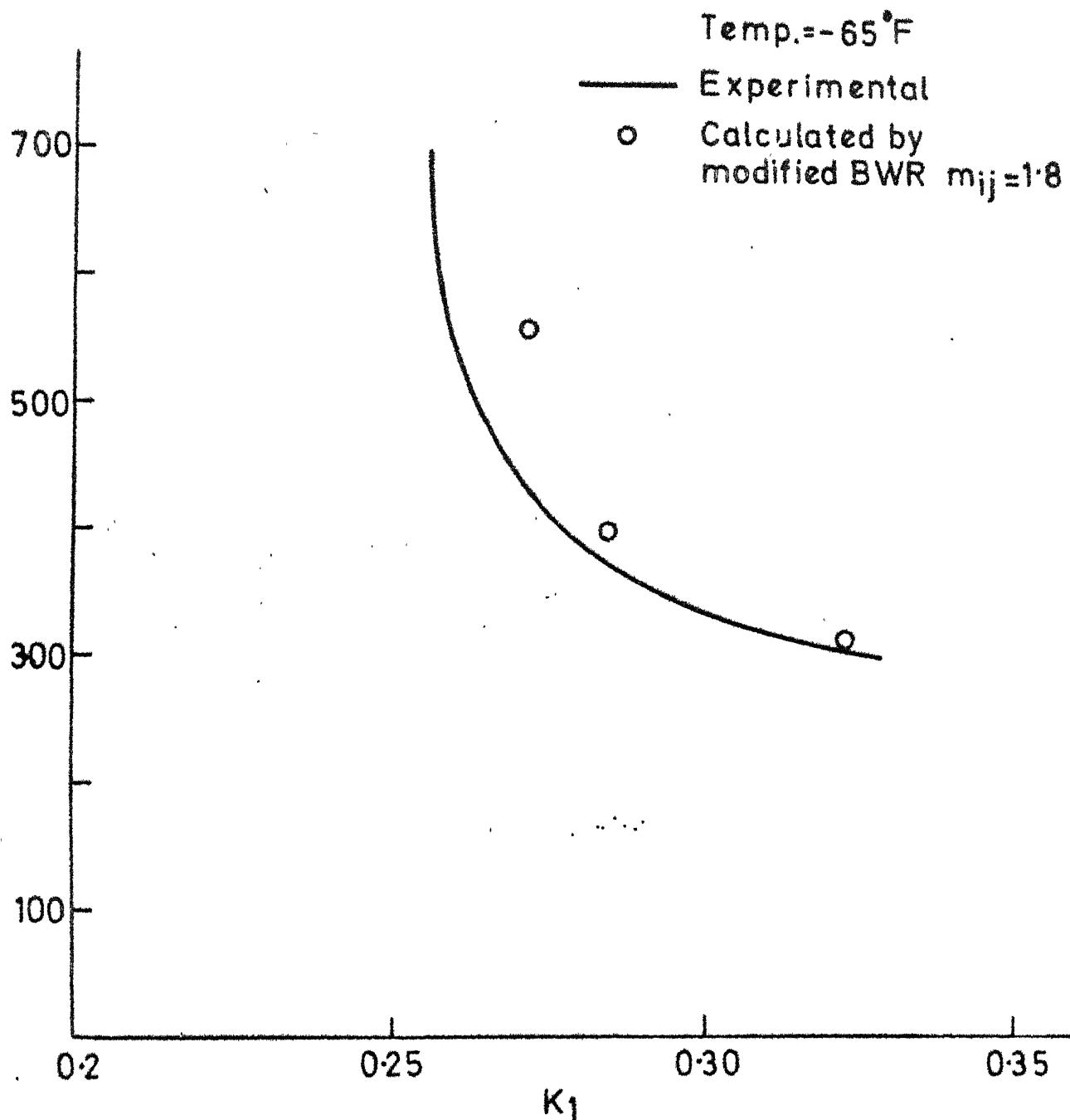


FIG. 8 EQUILIBRIUM VAPORIZATION RATIO $K = y/x$ FOR CO_2 METHANE

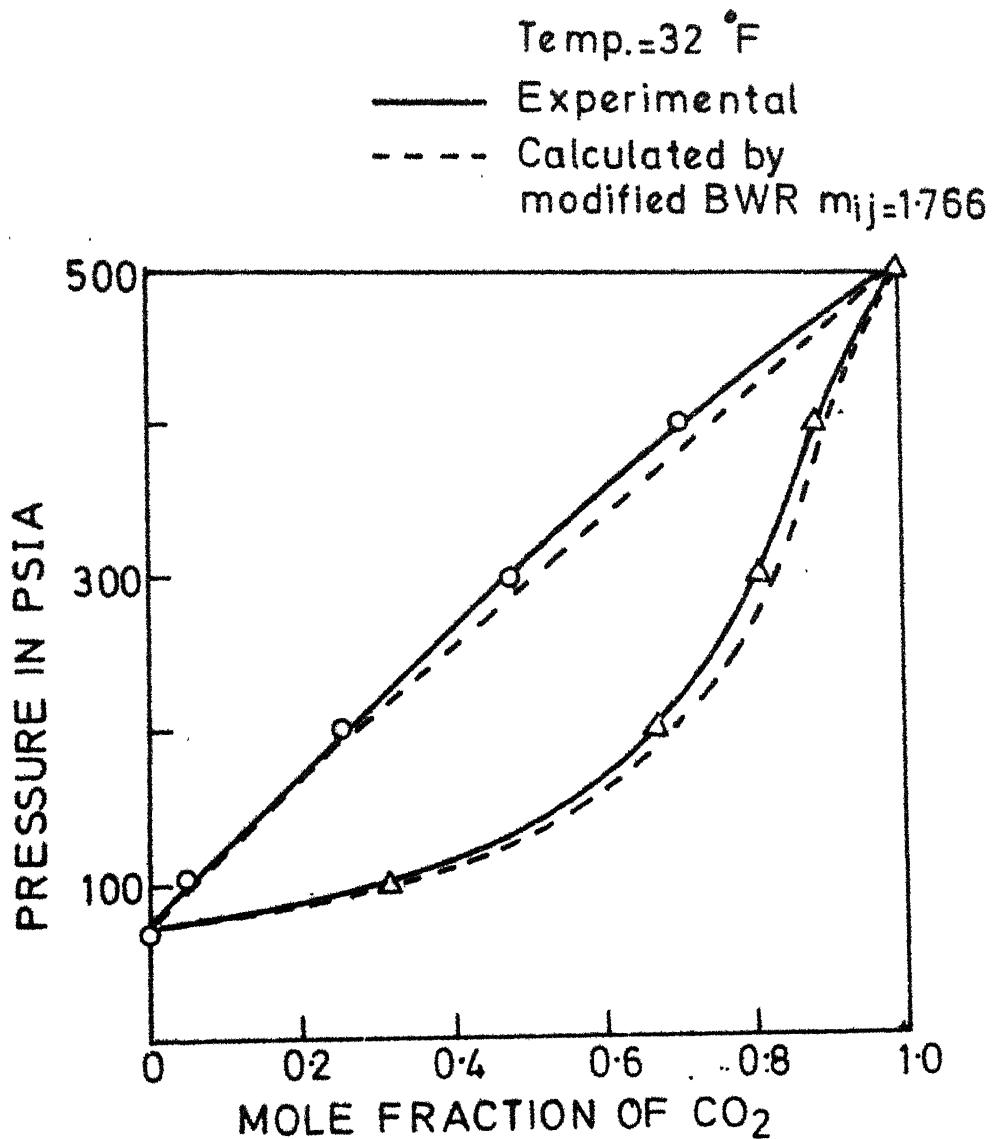


FIG. 9 EQUILIBRIUM VAPORIZATION RATIO $K=y/x$
FOR CARBONDIOXIDE-PROPANE MIXTURE

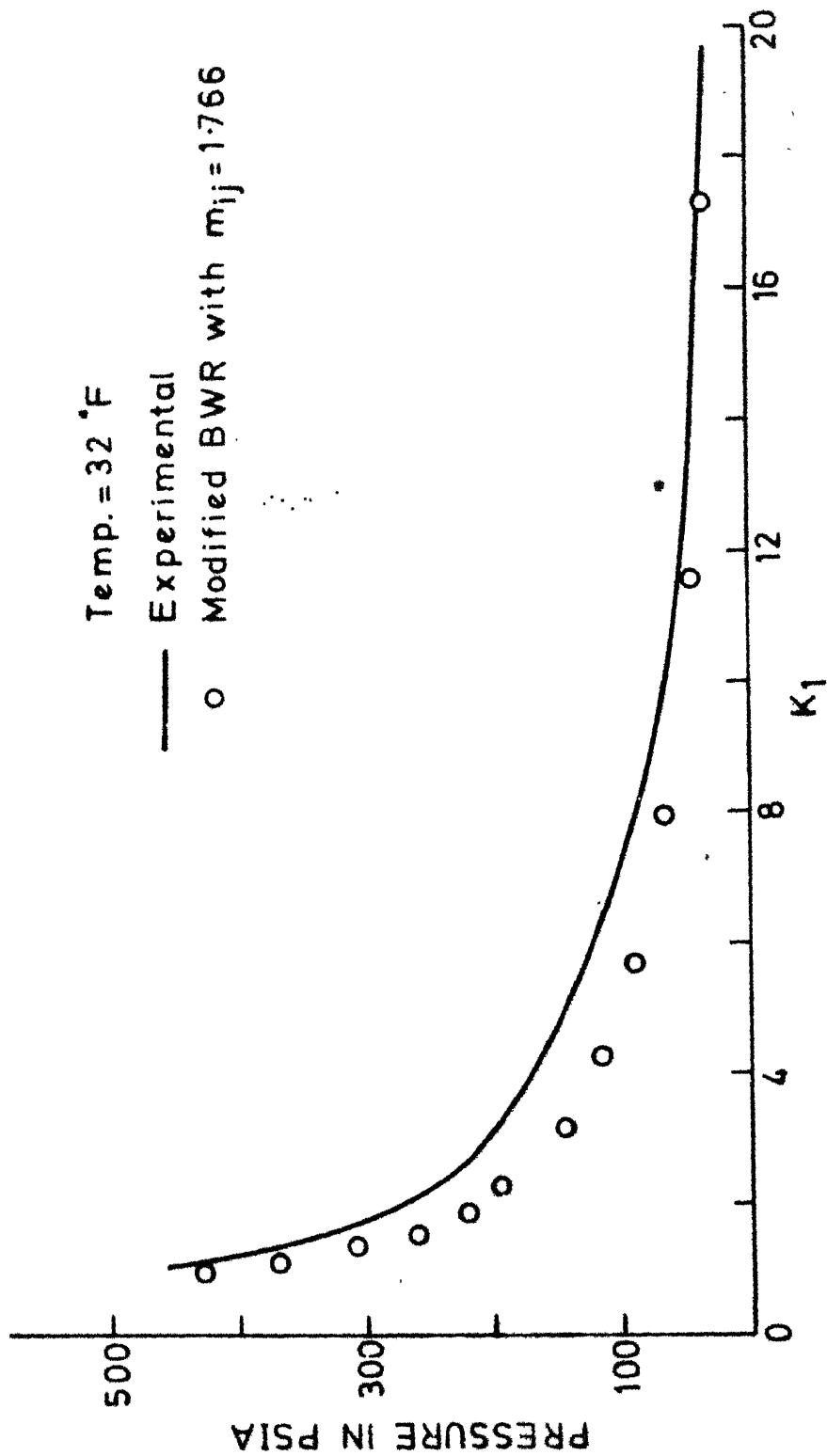


FIG. 10 VAPORIZATION EQUILIBRIUM RATIO $K = y/x$ FOR CARBON DIOXIDE PROPANE MIXTURE

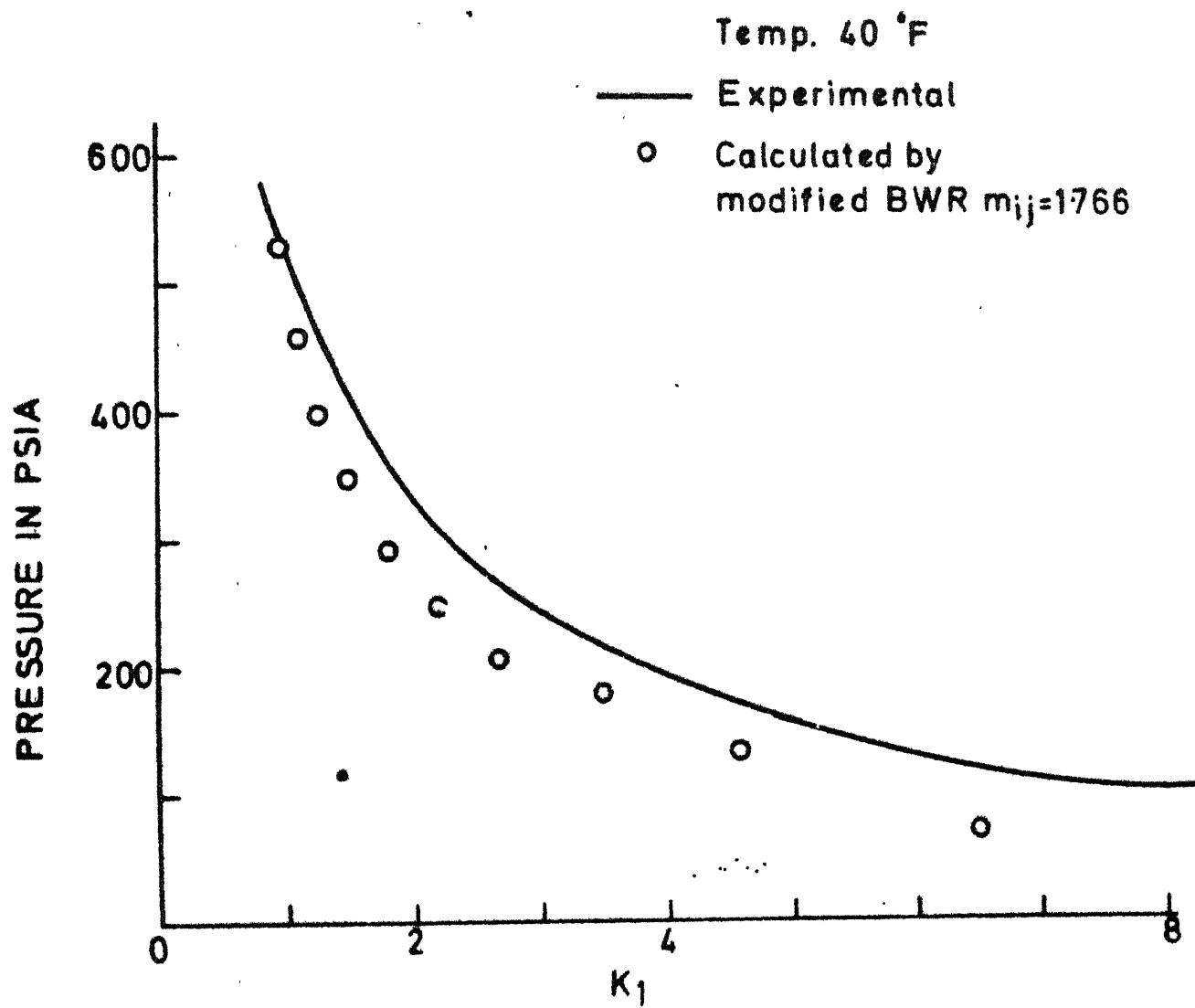


FIG.11 EQUILIBRIUM VAPORIZATION RATIO $K=y/x$ FOR $\text{CO}_2(1)$ -PROPANE MIXTURE

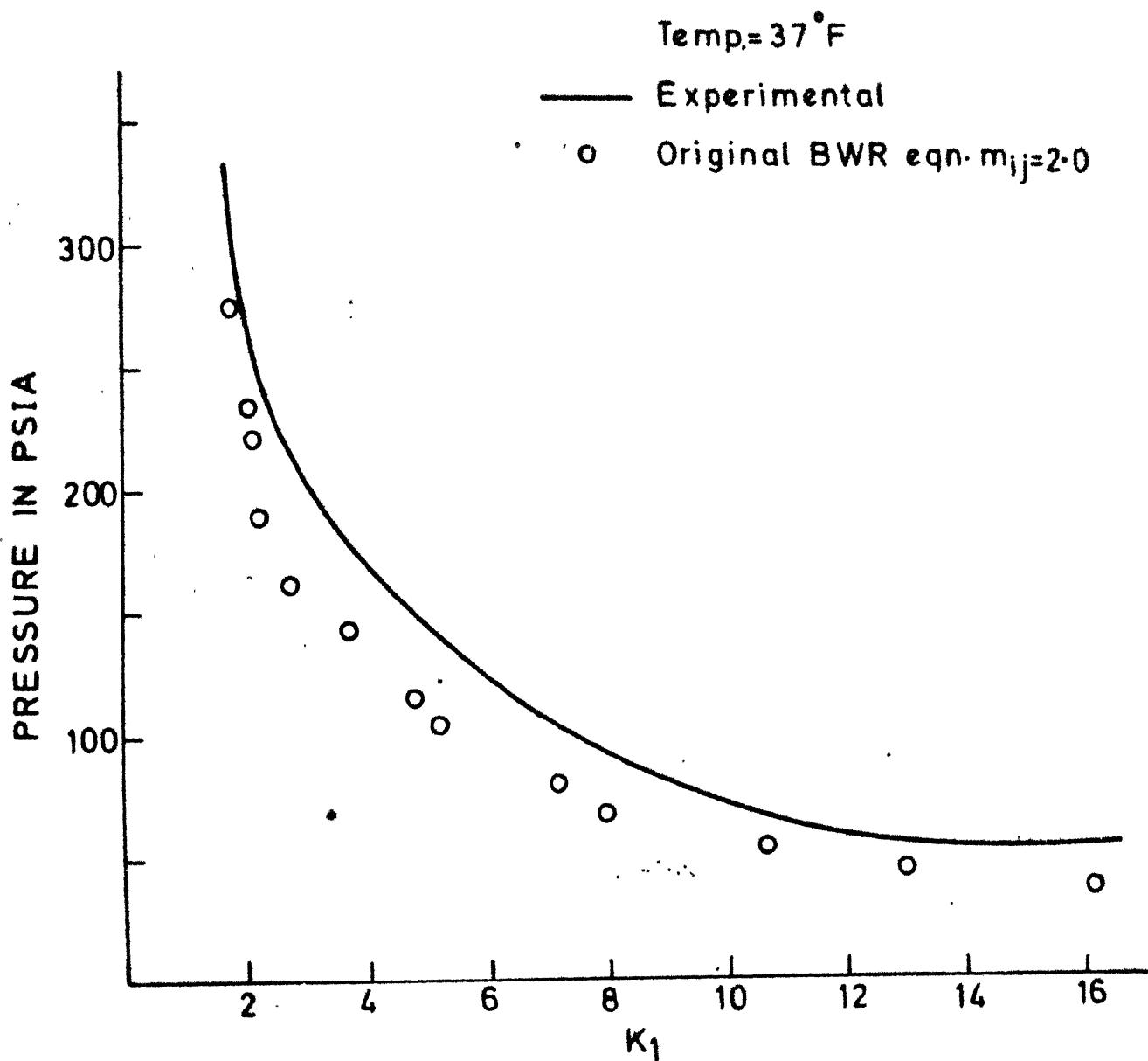


FIG. 12 EQUILIBRIUM VAPORIZATION RATIO FOR
CO₂-ISOBUTANE MIXTURE

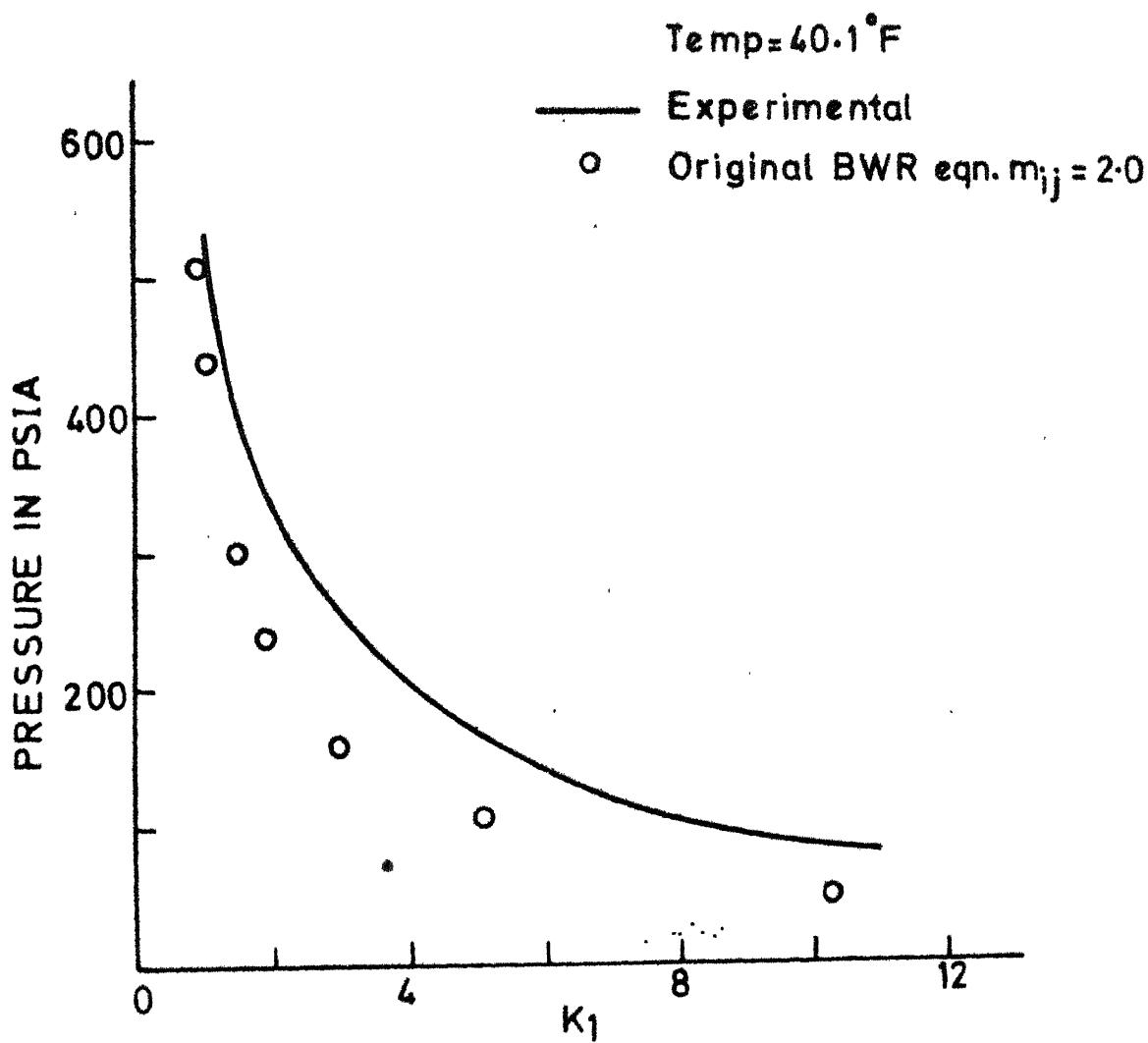


FIG. 13 EQUILIBRIUM VAPORIZATION RATIO $K=y/x$ FOR
 CO_2 -N PENTANE MIXTURE

269	101	0.14777E-1, 0 Z2=0, 0.001 TF001973=Z2)112,112,102
270	102	D1, 100, J=1, 400 D=0+C, J=0
271		PCALC=2*T*0+Z1*D*D+Z2*D*D*D+Z3*D**6+(C1*D*D*D/(T*T))* 2*(1,0+G1*A1*0.1*T*(D(-G1,1)*D+0))
272		DTRG=PCALC
273		DTRG2=ANS(DTRG)
274	103	TF001973)104,104,106
275	104	G1, T0, 107 C0, T0, 108
276	105	TF001973=0, 0.0011112,112,109
277	106	D=0+C, J=0
278	107	C0, T0, 140, J=0
279	108	G1, T0, 101 C0, T0, 102
280	109	R1(G1,1) D=0+C, J=0
281	110	R1(G1,1)
282	111	D=0+C, J=0
283	112	R1(G1,1)
284	113	D=0+C, J=0
285	114	R1(G1,1)
286	115	D=0+C, J=0
287	116	R1(G1,1)